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THE VARIOUS DETERMINATIONS OF THE E.M.F. OF THE CLARK CELL.

By Henry S. Carhart.

LATIMER CLARK in a communication to the Royal Society, May 30, 1872, made some general statements that are now known to be eminently true. He concludes the abstract of his paper as follows:[1] "The standard of electric potential is second only in importance to that of the standard of electric resistance; and the use of such a standard * * * admits of a variety of applications which it is believed will be found of great value in electrical research." It was many years before these statements were generally believed by electricians, but it has now come to be recognized that a good standard cell is of greater importance than a silver voltameter. The electromotive force of the Clark cell is now known with greater precision than the electrochemical equivalent of silver. The recent literature bearing on this constant, and its relation to the value of the mechanical equivalent of heat, render a recapitulation and reduction of its various determinations of considerable interest.

The earliest determination is that of Latimer Clark himself. It has the merit of being an absolute potentiometer method. The two elements of the determination were the measurement of a current and a resistance. The former was made by means of the electrodynamometer constructed for the British Association, or by the use of a sine galvanometer. The potential difference between

[1] Proc. Royal Soc., Vol. 20, p. 444, 1872.

the terminals of his current-measuring instrument was balanced against the E.M.F. of his standard cell. The resistance entering into the result was that of the electrodynamometer or the sine galvanometer. No current was taken from the standard, and its E.M.F. was equal to the product of the current and the resistance of the instrument.

The mean of eighteen trials with the electrodynamometer was 1.45735 at 15.5° C. The mean of thirteen with the sine galvanometer was 1.45621 at the same temperature. The final mean value was then 1.45678 at 15.5° C., or as given by Clark, 1.457 British Association units. But one B. A. unit equals 0.9866 international ohm. Therefore Clark's value reduced to present units at 15° is 1.4378.

So far as ascertained the next determination of the E.M.F. of the Clark cell was made by the writer in January, 1882, in Berlin.[1] The measurement was incidental to another investigation and was confined to a single cell belonging to the Physical Laboratory of the university. The method was the now well-known one of the silver voltameter. It is substantially the same as that employed by Clark, with the silver voltameter substituted for the electrodynamometer. The fall of potential over a known resistance was balanced against the E.M.F. of the standard cell. The results were not published till after Lord Rayleigh had made his determination of the electrochemical equivalent of silver in 1884. The published value was 1.434, but no corrections were made to reduce the E.M.F. to 15°, and the ratio of the Siemens unit of resistance to the ohm was taken to be $\frac{100}{106}$. It is perhaps worth while to make these corrections now when the requisite coefficients are well known. The following are the data:

Trial.	Temp. of Cell.	Res. in S. U.	Temp. of Res.	Silver Dep. per min.
1	18°	20	19°	0.0051 gm.
2	17	20	19	0.0051 "

$$\text{The current } I = \frac{0.0051}{0.001118 \times 60} = 0.07603 \text{ ampère.}$$

[1] Amer. Jour. Sci., Vol. XXXVIII., Nov., 1884.

The resistance box was correct at 20°. With a temperature coefficient of 0.0004 for German silver, 20 Siemens units equal 19.992 at 19°, and $19.992 \times 100/106.3 = 18.807$ ohms. Then

$$E = IR = 0.07603 \times 18.807 = 1.4299 \text{ volts.}$$

But the cell was at a temperature of 18° in the first trial and 17° in the second. The formula now used for temperature corrections of the Clark cell at the Reichsanstalt is

$$E_t = E_{15} - 119 \times 10^{-5}(t - 15) - 7 \times 10^{-6}(t - 15)^2.$$

This formula gives for the correction in the first case 0.0036, and in the second case, 0.0024. We have therefore

Trial 1	$1.4299 + 0.0036 = 1.4335$
Trial 2	$1.4299 + 0.0024 = 1.4323$
Mean at 15°	1.4329

No great weight is to be attached to this determination because the resistance used was not standardized, nor is it certain that its temperature was exactly indicated by the thermometer. The Clark cell was a large one containing a thermometer with its bulb within the contents of the cell. The balance with the silver voltameter was carefully maintained, the weighings were made after careful drying, and the deposit was washed in such a way as to avoid loss.

The next determination is that of Lord Rayleigh in 1884.[1] The method employed was a modified potentiometer method, the current being measured by the current balance which Lord Rayleigh used in his research on the electrochemical equivalent of silver. The value which Lord Rayleigh derived from all his determinations was 1.454 B. A. units at 15°. To reduce to volts the correction factor expressing the B. A. unit in terms of the ohm was introduced. The factor used by Lord Rayleigh was one B.A. unit equals 0.9867 ohm, giving the E.M.F. of the Clark cell 1.435 volts at 15°. If we employ the factor 0.9866 adopted by the British Board of Trade to convert B. A. units into ohms or volts, then Lord Rayleigh's value for the Clark cell is 1.4345 volts at 15°.

[1] Phil. Trans. Royal Soc., Part II., 1884.

Another determination with the silver voltameter is that of A. v. Ettinghausen.[1] He assumed Kohlrausch's second value for the silver equivalent, 0.0011183, and found for the E.M.F. of the Clark cell at 15.5°, 1.433 volts. If we correct for the electrochemical equivalent, 0.001118 instead of 0.0011183, and reduce to 15°, we have 1.434 volts.

A very elaborate investigation of the Clark cell was made by Glazebrook and Skinner in 1891–92.[2] The current was measured by the silver voltameter. Great precautions were taken to keep the standard resistance at a constant temperature. The mean of nine determinations was 1.4342 volts at 15°. To reduce to 15° the authors of the paper used the coefficient—0.00077. This gives a slightly smaller correction than the Reichsanstalt formula. Since the cell was always above 15°, the corrections are positive; the mean difference is two units in the fourth decimal place. Reduced to a common temperature coefficient, the final result of Glazebrook and Skinner's investigation is 1.4344 volts.

This is almost identical with the value derived from Lord Rayleigh's paper. He used for temperature corrections the coefficient —0.00082, which is equivalent to that of the Reichsanstalt formula for small ranges of temperature.

A good deal of interest attaches to the work done at the Reichsanstalt on Clark and Cadmium cells, and great confidence is felt everywhere in the results attained. In 1896 Kahle made an absolute measurement of the E.M.F. of the H-form of Clark cell by means of the Helmholtz absolute electrodynamometer.[3] This very elaborate instrument is fully described in Kahle's paper which is published as a contribution from the Reichsanstalt. For the E.M.F. at 0° C. he found 1.4488 volts. A direct comparison for the Clark at 0° minus the Clark at 15° gave $E_0 - E_{15} = 0.0166$. Hence at 15° the E.M.F. of the Clark cell found by Kahle is 1.4322 volts. The volt here corresponds to the international ohm, but not to the volt a sdefined in the legal definition of the Clark cell. The above value for the Clark cell has not been used by the Reichsanstalt.

[1] Zeitschrift für Elektrotechnik, 1884, XVI. Heft.
[2] Phil. Trans. Royal Soc., Vol. 183 A, 1892.
[3] Wied. Annal., Vol. 59, 1896, p. 573.

For about four years the Reichsanstalt has employed the following values:

Clark cell: 1.4328 int. volts at 15° C.
Cadmium cell: 1.0186 int. volts at 20° C.

The cadmium cell is the same as the Weston except that the $CdSO_4$ solution contains an excess of crystals, while the Weston is made with a solution saturated at 4° C. The manner in which the value 1.4328 for the Clark cell was obtained may be gathered from a paper by Jaeger and Kahle on "Mercury-Zinc and Mercury-Cadmium Elements as Standards of Electromotive Force." [1]

Three series of measurements were made with a large number of cells to determine the two ratios,

$$\frac{\text{Clark } 15°}{\text{Cadmium } 20°} \text{ and } \frac{\text{Clark } 0°}{\text{Cadmium } 20°}.$$

The results for the three series are shown in the table:

Date.	$\frac{\text{Clark } 0°}{\text{Cadm. } 20°}$	$\frac{\text{Clark } 15°}{\text{Cadm. } 20°}$	Clark 0° — Clark 15°
March, 1896	1.4227	1.4066	0.0164
Jan., 1897	1.42277	1.40676	0.01631
Nov., 1897	1.42280	1.40660	0.01650
Means	1.42277	1.40663	0.01642

The last column is easily obtained from the preceding two. The next step in fixing the E.M.F. of the Clark cell is Kahle's long series of determinations with the silver voltameter.[2] Assuming 0.001118 as the silver equivalent, he obtained for the Clark at 0° 1.44945, and for the cadmium at 20°, 1.01849. The ratio of these two numbers is 1.42313, or 0.00036 greater than the result of the direct comparison. Since the ratio of the silver voltameter measurements is affected by a greater uncertainty than the one directly observed, the difference is divided between the two electromotive forces obtained by the silver voltameter in proportion to their mag-

[1] Wied. Annal., Vol. 65, 1898, p. 926.
[2] Wied. Annal., Vol. 67, 1898, p. 1.

nitudes. The value for the Clark at 0° is thus reduced to 1.44923. Subtracting the fall of E.M.F. between 0° and 15°, and we have Clark at 15° equals 1.4328 volts.

Similarly the Cadmium cell becomes 1.0186 at 20°. While this method is something of an improvement on the old one with the silver voltameter, it is yet fundamentally the same and leaves much to be desired.

A year ago Professor Lindeck and myself made several series of observations at the Reichsanstalt to redetermine the ratios between the Clark at 0° and at 15° and the cadmium at 20°. A large number of cells, new and old, were used. The precautions taken to maintain a constant temperature during a series of observations proved highly satisfactory. The comparisons were made rapidly by means of the well-known compensating apparatus devised at the Reichsanstalt and made by Wolff in Berlin. Three series of comparisons gave as a mean for the ratio Clark 15°/Cadmium 20°, 1.40679.[1]

Nine Clark cells were then placed in a petroleum bath and completely surrounded by pounded ice for five days. Eight series of comparisons gave, Clark 0°/Cadmium 20° = 1.42283.

These new ratios of the Clark at 0° and at 15° compared with the Cadmium at 20° give, Clark 0° — Clark 15° = 0.01634. Then by the method of reduction used by Dr. Kahle, 1.44929 — 0.01634 = 1.43295 at 15°.

The above new ratios are published in the last "Thätigkeitsbericht" of the Reichsanstalt, but the recommendation is made that the old value for the E.M.F. of the Clark cell at 15°, viz., 1.4328 should be retained. This recommendation does not appear to be quite reasonable, since the new ratios are derived from more concordant series of observations than the old ones, and their application to Kahle's results from the silver voltameter deposits gives a value very near 1.433 volts at 15°.

During the summer of 1899 an absolute determination of the E.M.F. of the Clark cell at 15° was made by myself and Dr. Guthe. The fall of potential over a known resistance was compared by a potentiometer method with the E.M.F. of two Clark

[1] Zeitschrift für Instrumentenkunde, June, 1900, p. 176.

cells of the modified H-form joined in series.[1] The current was measured by our absolute electrodynamometer of simple construction.[2] The resistance was determined in terms of two one-ohm coils with Richsanstalt certificates. The result of three determinations was E.M.F. of Clark at 15° is 1.4333 volts.

This value we do not consider final. The measurement may be made under improved conditions, and the suspended coil wound on a hard rubber cylinder was probably not exactly circular in section. A new porcelain cylinder with a guaranteed external diameter has been obtained from the Royal Porcelain Works in Berlin through the courtesy of Mr. Louis J. Magee, of that city. It has not yet been mounted in the electrodynamometer. A large porcelain cylinder will also be tried for the fixed coil.

Finally an interesting side light has been thrown on the value of the E.M.F. of the Clark cell by the fact that Griffiths' determination of the mechanical equivalent of heat by an electrical method gave a result larger than Rowland's by a constant small amount of one part in 400 or 500. Since the E.M.F. enters the result as the square, an error in the E.M.F. of the Clark cell of about one part in 1,000 would explain the discrepancy. This would mean a value of a little less than 1.433 instead of 1.434.

In a recent communication to the Royal Society on a new determination of the mechanical equivalent of heat by an electrical method differing from that of Griffiths, Barnes, of McGill University,[3] points out that his result is higher than those obtained by direct mechanical methods. He attributes the discrepancy to an incorrectness in the assumed value of the E.M.F. of the Clark cell. A value of 1.43325 instead of 1.4342 volts causes the discrepancy to disappear.

In the light of such facts it is interesting to place before us a tabular view of the several determinations which I have briefly described, and which I have reduced to common terms:

[1] PHYS. REV., Vol. IX., No. 5, 1899, p. 288.
[2] PHYS. REV., Vol. VII., No. 39, 1898.
[3] London Electrician, Oct. 19, 1900.

Observer.	Date.	Method.	Result.
Clark.	1872	Absolute.	1.4378
Carhart.	1882	Silver Voltam.	1.4329
Rayleigh.	1884	Absolute.	1.4345
Ettinghausen.	1884	Silver Voltam.	1.434
Glazebrook & Skinner.	1892	" "	1.4344
Kahle.	1896	Absolute.	1.4322
Jaeger & Kahle.	1898	Silver Voltam.	1.4328
	1899	" "	1.4329
Carhart & Guthe.	1899	Absolute.	1.4333

If we omit Clark's determination, because his cells set up with boiled zinc and mercurous sulphates are not comparable with the others, only three absolute determinations have been made. The mean of these is 1.4333 volts at 15°.

A study of the above table can hardly fail to produce the conviction that the E.M.F. of the Clark cell at 15° C. is nearer 1.433 than 1.434 volts.

UNIVERSITY OF MICHIGAN, Dec. 1, 1900.

VELOCITY OF IONS DRAWN FROM THE ELECTRIC ARC.

By C. D. Child.

THERE appeared in a recent number of the PHYSICAL REVIEW[1] an article by the present writer offering an explanation of the electric arc on the assumption that the current in the arc is carried by ions. In order to account for the fall of potential through the arc it was necessary to assume in that explanation that the positive ions move more rapidly than the negative under similar conditions. There appeared to be some difficulty in such an assumption, since in all cases which had been studied the negative ions had been found to move the more rapidly.

Method here used.—Since the publication of that article a method of investigating the arc further has been tried. The method is a modification of one suggested by Prof. J. J. Thomson[2] and its application to the study of the velocity of ions drawn from a flame has already been published.[3] In that article it was shown that in the case of a very large supply of ions of both kinds a comparison of the velocities of the negative and positive ions could be made by simply comparing the positive and negative rates of discharge from the source of ionization to bodies near it. If the discharge takes place from one regular surface to a second regular surface, it is possible to find the exact values of the velocities. The arc, however, is not susceptible of analytical treatment. Moreover in this case the chief point of interest is to prove that the positive ions move the more rapidly and it is of secondary interest to show exactly what that velocity is.

The conclusion of the discussion previously given may be stated as follows. Let Fig. 1 indicate the cross section of two surfaces.

[1] PHYS. REV., 10, p. 151.
[2] Phil. Mag. (5), 47, p. 265.
[3] PHYS. REV., 12, p. 65.

Let there be in A a supply of both positive and negative ions. If the other surface B is charged positively, negative ions will be drawn toward B. If B is negative, positive ions will be thus drawn. If the supply of ions of both sorts in A is very large as compared with number drawn out, the current carried by the positive ions will be larger, if the positive ions move the more rapidly; that carried by the negative, if the negative ions move the more rapidly. This will also be true whether the surfaces A and B are regular or irregular.

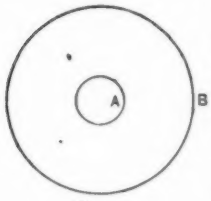


Fig. 1.

The instruments used and the methods of measuring the rates of discharge were the same as those described in the article on the velocity of ions drawn from a flame.

There was an added difficulty in this case due to the fact that the potential of the arc could not be made very much different from that of the ground. The arc was supplied with current from a storage battery of thirty cells. This battery and its connections were insulated as far as possible, but the fumes from the acid made the insulation poor. When the attempt was made to raise the potential of the arc above that of the ground the water battery used for the purpose became quickly polarized. Consequently the arc was kept at near the potential of the ground and the metal to which the discharge took place was charged, the water battery being between the charged metal and the electrometer or galvanometer. In this way the instrument used to measure the rate of discharge was always near zero potential.

The current flowing from the arc to the metal will be called the positive current. This current is carried by positive ions. The current in the opposite direction is carried by negative ions and is called the negative current. The radius of B, Fig. 1, will be indicated by b and the difference of potential between A and B by V_b.

In the first experiments a small piece of sheet iron 1 cm. square was placed 1 cm. from the arc, and the current to this from the arc was measured by a galvanometer. It was found that the movements of the arc produced great changes in the rate of discharge from it. The positive current appeared to be the greater, but one

could not be absolutely certain. To test this a reversing key was placed in the circuit and so operated by a pendulum that the potential of the charged plate was reversed once in .7 sec. Since the period of the galvanometer was 12.6 sec. for a complete swing, the needle did not move far from its mean position, when the potential of the charged metal was constantly reversed. By this means it was possible to determine the difference between the two currents.

Since the reversing key might send the current longer in one direction than in the other, the current was occasionally reversed before it was brought to the key described above, and the arrangement was so adjusted that this occasional reversal had no effect on the reading.

In the first trial a small carbon connected to ground was placed in the arc, and it was then assumed that the protential of the arc was zero. As near as could be estimated the average positive current was 3.1×10^{-8} ampère, the negative 1.8×10^{-8} ampère. The difference as shown by the reversing key 1.3×10^{-8} ampère.

In other experiments where a cylinder was placed about the arc the fluctuations of the arc had less effect on the rate of discharge and in most cases this reversing key was not needed.

Lest some error was being made in the sign of the current, the arc was replaced by the flame from a Bunsen burner. It has already been shown that with this the negative current is the greater, so that with the flame the current should be greater in one direction and with the arc in the other. On testing it this was found to be the case.

The Potential of the Arc Varied.—There was in this the possibility of error, since the potential of the arc was assumed to be the same as that of the small carbon inserted in it. One might think that possibly the arc did not assume the potential of the carbon, or that the discharge came from one of the carbons of the arc. To make sure that no error was being introduced in this way the rate of discharge was noted when different parts of the arc were grounded, or, what amounted to the same thing, when different points on a shunt placed about the arc were grounded. And instead of placing a small piece of iron near the arc a cylinder 2 cm. long and 4.5 cm. in diameter was used. This cylinder was made

of tin. The arc was placed in the center of this as nearly as possible. Above and below this, but insulated from it were cylinders of the same diameter. These were kept at the same potential as the central cylinder and served the same purpose as an ordinary guard ring. The arc and cylinders were vertical. The difference of potential between the ring and the ground was 95 volts.

With the ground at the negative carbon the negative current was 1.1×10^{-8} ampère, and the positive 1.2×10^{-8}.

With the ground $\frac{1}{4}$ of the way from the negative to the positive carbon the negative current was $.9 \times 10^{-8}$ ampère, the positive 1.3×10^{-8}.

With the ground half way between the positive and negative carbon the negative current was $.85 \times 10^{-8}$ ampère, the positive 1.5×10^{-8}.

With the ground $\frac{3}{4}$ of the way to the positive carbon, the negative current was $.8 \times 10^{-8}$ ampère and the positive 1.7×10^{-8}.

With the ground at the positive carbon the negative current was $.6 \times 10^{-8}$ ampère, the positive 1.9×10^{-8}.

It is seen that in every case the positive current was the greater. According to Mrs. Ayrton[1] the difference of potential between the negative carbon and the arc is about $\frac{1}{4}$ of the difference of potential between the two carbons, so that the arc will be practically at zero when the ground on the shunt is $\frac{1}{4}$ of the way from the negative to the positive carbon. In the rest of the work the ground was kept at that point.

Position of the Arc Varied.—During this experiment the arc had been on the level with the center of the cylinder to which the discharge was taking place. The position of the arc was then raised 1.5 cm. The lower carbon was negative and was nearer to the cylinder. It was found that in this position the currents were much smaller but that the ratio between the two currents was practically the same as before. The positive current was 4.4×10^{-9} ampère, the negative 2.2×10^{-9}.

The current through the arc was then reversed so that the cylinder was nearer the positive carbon, and the currents were practically the same as before this reversal. This would indicate that

[1] Lond. Elec., 41, p. 720.

the discharge was from the arc itself and not from either of the carbons, or at least was not from one carbon more than from the other.

Potential of Vapor from Arc Studied.—It has been stated by some observers[1] that the vapors from the arc are charged and it was thought that this might be affecting the results here given. A cylinder 5 cm. long and 4.6 cm. in diameter was accordingly placed about the arc and the potential which this assumed when insulated was noted. The potential of the arc was also determined roughly by means of a small carbon placed in the arc. The potential of the arc has been studied thoroughly by Mrs. Ayrton, so that no attempt was made to do more than to show that the behavior of the arc here used was normal.

The potential was found by grounding different points on the shunt about the arc until a point was found which caused the small carbon to assume zero potential. The potential of the arc fluctuated through a few volts, but the average potential was practically the same which others have found. The potential of the cylinder about the arc was found in the same way, and was found to be somewhat different from that of the arc.

To test this further one pair of quadrants of the electrometer was connected to the cylinder about the arc and the other pair to the small carbon placed in the arc. It was then found that the cylinder assumed a potential between that of the small carbon and that of the upper carbon of the arc. Thus if the upper carbon was positive the cylinder was positive as compared with the small carbon, the difference being about 14.5 volts. If the upper carbon was negative the cylinder was negative, the difference being 7 volts. The difference of potential between the small carbon and positive terminal was 23 volts and that between the small carbon and the negative terminal 9 volts.

The potential of the cylinder about the arc was also examined when salts were placed in the arc and when tin was placed in one of the carbons which had been hollowed out, and in every case the cylinder was found to have a potential between that of the arc and that of the upper carbon of the arc.

[1] Wied. Ann., 40, p. 332.

This effect is very similar to that found by Merritt and Stewart[1] except that in their case the potential of the vapor drawn from the arc had the same sign as the lower carbon of the arc. The cases, however, are sufficiently different to account for the different results. As shown bv Merritt and Stewart with their apparatus the arc was enclosed and convection currents carried the vapors from the arc down by the side of the enclosure and up again past the lower carbon and were drawn off into the space where they were examined, so that the lower carbon might easily give its potential to the vapor. In the case here described there was no chance for the ionized vapors to be carried down and receive the potential of lower carbon. They were carried up past the upper carbon and out into the room, so that they had the potential of the upper carbon.

However, this evidently has no bearing on the matter in hand. This effect may be reversed by reversing the current in the arc while the rate of discharge to a charged ring about the arc is independent of the direction of the current in the arc.

Effect not Due to Ultra-violet Light.—The possibility suggested itself that the rate of discharge from the arc was being modified by the ultra-violet light of the arc. This seemed highly improbable since the cylinders surrounding the arc were of tin, but to make sure concerning it a cylinder of wire gauze 9 cm. long and 4.5 cm. in diameter was placed about the arc. This screened off about one-half of the light. About this a cylinder 6 cm. in diameter and 2 cm. wide was placed. The inner cylinder was charged to 100 volts, the outer one was connected to the electrometer. A small charge passed to the outer ring whether the inner cylinder was charged positively or negatively, but scarcely $\frac{1}{100}$ of the amount necessary to account for the difference between the positive and negative discharge which has been noted.

But it was possible to show even more clearly that the effect was not due to ultra-violet light. A small cylinder 4.5 cm. in diameter and 6 cm. wide was placed about the arc and grounded. About this a larger cylinder 6 cm. in diameter and 2 cm. wide was so placed that it was entirely screened from the light of the arc, so

[1] PHYS. REV., 7, p. 141.

that light could not in any way affect the discharge taking place from it. This outer ring was charged and it was found that discharge still occurred and that when the cylinder was charged negatively the rate of discharge was greater than when it was charged positively. This discharge is no doubt due to the fact that some of the lines of force from the outer cylinder bend around the edges of the inner one and draw out ions from the neighborhood of the arc. In this case as in others the discharge produced by the positive ions is the greater.

If there is here any such effect as Lenard [1] has recently described, it would not explain the fact that the current is greater in one direction than in the other.

Current in the Arc Varied.—The effect of varying the current in the arc was then tried and the results are given in the following table. The arc was here surrounded by a cylinder 4.5 cm. in diameter and 2 cm. wide, with guard cylinders on each side. V_b was 95 volts.

TABLE I.

1 Current in Arc.	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
4.5	1.76×10^{-8}	$.83\times10^{-8}$	2.1
6.5	2.28 "	1.16 "	1.96
8.5	2.4 "	1.25 "	1.92

Column 1 gives the current through the arc in ampères. Column 2 the rate of discharge in ampères when the surrounding cylinder was negative, column 3 when it charged positively, and column 4 the ratio between these two values.

In general the rate of discharge becomes greater as the current in the arc is increased, but in all cases the discharge carried by positive ions is the greater, and the variation in the ratio between two rates of discharge is such as might easily be caused by the fluctuations of the arc. In the following experiments the current in the arc was kept as near 5 ampères as was practical :

Diameter of Cylinders Varied.—Cylinders with different diameters were then used and the results are given in Table 2. The cylin-

[1] Drude Ann., 1, p. 486.

ders were 2 cm. in width and in each case guard cylinders were placed above and below them. V_b was 95 volts.

TABLE II.

1 b	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
2.25	17.6×10^{-9}	8.32×10^{-9}	2.1
3.1	4.63 "	2.03 "	2.28
4.5	1.06 "	.59 "	1.8
6.3	.307 "	.17 "	1.8
9.	.122 "	.061 "	2.

Column 1 gives the radius of the surrounding cylinder. The other columns are the same as in the previous table. The variations in the ratios between the two currents are probably due entirely to fluctuations in the current of the arc.

V_b Varied.—Table 3 gives the values of the currents for different values of V_b. In this case b was 2.3 cm. and the width of the cylinder was 2 cm. Column 1 gives the value of V_b. The other columns are the same as in the previous tables.

TABLE III.

1 V_b	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
50	4.4×10^{-9}	2.2×10^{-9}	2.
95	17.6 "	8.37 "	2.1
175	52.8 "	24.2 "	2.18
251	88. "	44. "	2.

Theory of Discharge between Cylinders.—Thus far we have only found the comparative velocities of the positive and negative ions. It will be of interest to find even the approximate values in absolute units. If we could treat of the arc as a cylinder of infinite length surrounded by a second such cylinder, the problem could be solved mathematically; or if it were a sphere surrounded by a second sphere with the potential varying according to the same law in all directions, the problem could be solved. But it is neither of these. The arc itself might be treated as a sphere, but the presence of the carbons causes the potential to vary quite differently in different directions. It is, however, of some interest to compute the

velocity on the assumption that one or the other of the above cases applies, and the following is a treatment of the case on the assumption that the arc is an infinite cylinder. To do so is not quite as unreasonable as might at first sight appear, since we have only used a small part of the outer cylinder opposite the arc.

The mathematical treatment is similar to that given by Professor Thomson[1] for the case of discharge between plates. Let the space within A, Fig. 1, by supplied with both positive and negative ions and let ions of one sign only be drawn from A to the cylinder B. Let B be charged negatively. Then the ions in this space will be charged positively. Let V be the value of the potential at any point, e the charge carried by each ion, n_1, the number of positive ions per unit volume, k_1, the velocity of the positive ions for unit potential gradient, r, the distance from the center of the cylinders, i, the current through unit area and we have

$$\frac{d^2V}{dr^2} + \frac{1}{r}\frac{dV}{dr} = -4\pi n_1 e$$

and

$$k_1 n_1 e \frac{dV}{dr} = -i_1 = -\frac{I_1}{r}$$

where I_1 is the value of i_1 when $r = 1$.

Or

$$\frac{dV}{dr}\frac{dV^2}{dr^2} + \frac{1}{r}\left(\frac{dV}{dr}\right)^2 = \frac{4\pi I_1}{k_1 r}.$$

Integrating this expression we have

$$\frac{dV}{dr} = -\sqrt{a + \frac{C^2}{r^2}} \quad \text{where} \quad a = \frac{4\pi I_1}{k_1}.$$

By a course of reasoning similar to that given in the PHYSICAL REVIEW, 12, p. 65, it can be shown that $\frac{dV}{dr}$ is very small at the surface of A. Let r_0 be the radius of this cylinder and assume that $\frac{dV}{dr} = 0$ when $r = r_0$, and the above equation becomes

[1] Phil. Mag., (5), 47, p. 265.

$$\frac{dV}{ar} = -\sqrt{a}\sqrt{1-\frac{r_0^2}{r^2}}.$$

If this be integrated we have

$$V = -\sqrt{a}\left\{\sqrt{r^2-r_0^2} + r_0 \sin^{-1}\left(\frac{r_0}{r}\right)\right\} + C'.$$

If $V = 0$ when $r = r_0$,

$$C' = \frac{r_0\pi\sqrt{a}}{2}$$

and

$$V = -\sqrt{a}\left\{\sqrt{r^2-r_0^2} + r_0\left[\sin^{-1}\left(\frac{r_0}{r}\right) - \frac{\pi}{2}\right]\right\}.$$

If higher powers of $\frac{r_0}{r}$ may be omitted

$$V = r\sqrt{a}\left\{1 + \tfrac{1}{2}\frac{r_0^2}{r^2} + \cdots - \frac{\pi}{2}\frac{r_0}{r}\right\}.$$

Substituting the value of a, letting b be the value of r, and V_b the corresponding value of V, solving for k_1 we have

$$k_1 = \frac{4\pi I_1 b^2\left\{1 + \tfrac{1}{2}\frac{r_0^2}{b^2} + \cdots - \frac{\pi}{2}\frac{r_0}{b}\right\}^2}{V_b^2}.$$

Or in the practical system of units

$$k_1 = \frac{36\pi \times 10^{11} I_1 b^2\left\{1 + \tfrac{1}{2}\frac{r_0^2}{b^2} + \cdots - \frac{\pi}{2}\frac{r_0}{b}\right\}^2}{V_b^2}.$$

If k_2 is the velocity of the negative ions for unit potential gradient, a corresponding expression for k_2 may be found.

Values Found for k_1 and k_2.—Using the data in Table II. and remembering that the total current to the cylinder is 2π times the width of the cylinder times I, we find that when b is 2.25 cm. and V_b 95 volts the theory gives us 4.1 cm. per volt per cm. for k_1, and 1.95 cm. for k_2. As b becomes larger the values of k_1 and k_2 become smaller. For example when b is 4.5 cm. k_1 is 1.47 cm., and k_2 .82 cm. This corresponds to the similar case with ions drawn from a flame and

is what might naturally be expected. The values here found, however, are somewhat smaller than the corresponding values of the ions from a flame. If there were any difference, one would expect the ions from the flame to move with smaller velocity, since the arc is hotter. But the assumption made in deriving the formula given above is too far from the truth to make the numerical results of much importance. It is scarcely worth while to compare the values found for different distances with one another or with the corresponding values for the ions from a flame.

Agreement of Observations with Theory. According to the theory the current should vary inversely as the cube of the radius of the surrounding cylinder. Since the area of the cylinder itself varies as the radius the total current received should vary inversely as the square of the radius. This agrees fairly well with observed data. The current, however, decreases somewhat more rapidly than it should. This may be due either to the fact that the actual conditions do not correspond closely to the assumed conditions, or possibly to a slower motion of the ions as they move further from the arc.

The current should also vary as the square of V_b. It does not, however, vary as rapidly as this, probably again because of the lack of agreement between the assumed and the actual conditions. The increase in the rate of discharge when the current in the arc is increased can be explained by the increase in r_0, the radius of the arc itself, or on the assumption that the velocity of the ions becomes greater as the arc becomes hotter. Further work will be necessary before a full explanation of what has been observed can be given.

Vapors Rising from the Arc.—Thus far the ions have been drawn directly from the arc. One of the experiments performed by Merritt and Stewart[1] indicated that in the vapors rising from the arc the negative ions move the more rapidly. It seemed well to make some further test of this and the following was tried. The arc was placed in a horizontal position and above it was placed a sheet of tin which was connected to the ground. In this there was an opening 1 cm. in diameter directly above the arc. In the vapors carried up through this by convection currents there was a copper wire and

[1] PHYS. REV., 7, p. 143.

about this a cylinder 4.5 cm. in diameter and 2 cm. long. We here again have conditions similar to those indicated in Fig. 1, *i. e.*, a space filled with ions of both signs and about this a space filled with ions of one sign only. We have not so great a supply of ions as in the arc, and yet may reasonably suppose that there were many more in the rising vapor than were drawn out to the surrounding cylinder.

Under these conditions the rate of discharge was found to be greater when the surrounding cylinder was charged positively. No explanation for this has suggested itself other than that this greater discharge was caused by the more rapid motion of the negative ions. This agrees with the conclusion of Merritt and Stewart, although it was scarcely what was to be expected from the work on the arc itself.

It would seem as if of the ions drawn directly from the arc the positive ones move the more rapidly, but that these quickly lose this rapidity of motion and come to move slower than the negative ones. It would be of interest to investigate the change from the condition where the positive ions move the more rapidly to that where the negative ions do, but the present writer has not yet been able to do this.

Arc Between Metals.—Lecher[1] observed in 1888 that the fall of potential at the positive terminal of an arc established between metals was no greater than that at the negative terminal. My own observations indicate that the fall of potential at the positive terminal is slightly less than the other. If this be so, in order to explain it on the hypothesis that the current is carried by ions it is necessary to assume that in such cases the negative ions move the more rapidly. This fact affords a test for the theory. The rates of discharge from the arc between metals was accordingly examined and in every case it was found that when the cylinder surrounding the arc was charged positively the rate of discharge from it was greater than when it was charged negatively indicating that the negative ions here move the more rapidly.

The data found in this work are given in Table IV. Column 1 gives the metal used. Column 2 the rate of discharge when the

[1] Wied. Ann., 33, p. 609.

surrounding cylinder was charged negatively. Column 3 when charged positively. Column 4 the fall of potential at positive terminal in volts. Column 5 that at the negative, V_b was 94 volts b was 2.25 cm. and the width of the cylinder 2 cm. The ground in using the metals was at the middle point of the shunt about the arc. The current through the arc was about 6 ampères.

TABLE IV.

1 Name of Metal.	2 Positive Current.	3 Negative Current.	4 Fall of Potential at the + terminal.	5 Fall of Potential at the − terminal.
Zinc.	$.88 \times 10^{-8}$	1.32×10^{-8}	12	14
Iron.	2.2 "	2.64 "	13	15
Copper.	2.2 "	3.08 "	11	14
Carbon.	1.76 "	.83 "	23	9

Salts in the Arc.—Experiments were also performed with carbons hollowed out and filled with salts. The salts, however, soon evaporated so that the condition of the arc was continually varying and made quantitative measurements impossible. Na_2CO_3 and $CuSO_4$ were tried and when the arc was first started it behaved in respect to the potential of the arc and to the rate of discharge to the surrounding cylinder as an arc between metals, but in a few seconds it changed over to the condition of the ordinary arc in both these respects. This indicates that at first, when the vapor of the salt was abundant in the arc, the negative ions moved the more rapidly, and that when this vapor became less abundant the positive ions moved the more rapidly.

Oxy-hydrogen Flame.—An oxy-hydrogen flame playing on a piece of carbon connected to the ground was put in the place of the arc. When the flame was as hot as it could be made the results were the same as with the arc between carbons. When the flame was not so hot, or when there was no carbon in the flame, but the flame was grounded by grounding the burner, the effect was the same as with a Bunsen burner. The positive current for $b = 4.5$ cm., width of cylinder $= 2$ cm. and $V_b = 95$ volts was 3.1×10^{-8} ampère, the negative 2.8×10^{-8} ampère.

Pencils of iron, copper, zinc, aluminum and platinum were placed in the flame, but in no case was the effect the same as that observed

with the carbon. This proves but little, however, since in all these cases the metals melted before observations of value could be taken, and long before they reached the temperature which the carbon assumed.

Summary.—The preceding work may be summarized as follows:

A study of the rate of discharge from an arc to a neighboring body shows that under varying conditions of difference of potential distance and current in the arc itself the positive ions drawn out from the arc move more rapidly than the negative ones. This is not to be explained as an effect due to ultra-violet light or any phenomena previously studied.

The positive ions from a carbon placed in an oxy-hydrogen flame also move the more rapidly. In cases of an arc between metals the negative ions move the more rapidly.

While this work does not prove that the positive ions in the arc itself move more rapidly than the negative ones there, it is in every respect consistent with such a hypothesis, and it shows that it is possible for the positive ions to do so. The question why the positive ions here show this peculiarity is, of course, entirely unanswered. In all the cases so far studied we have carbon and also a very high temperature. It would at present be useless to speculate as to whether this phenomenon is to be ascribed to one or the other of these facts or to some one entirely different. The author hopes in time to publish further experiments bearing on this point.

COLGATE UNIVERSITY, January 25, 1901.

A SPECTROPHOTOMETRIC STUDY OF THE HYDROLYSIS OF DILUTE FERRIC CHLORIDE SOLUTIONS.

By B. E. Moore.

1. General Theory.
2. Theory Applied to Experimental Conditions.
3. Theory Applied to Dilute Ferric Chloride Solutions.
4. Use of Apparatus and Errors Involved.
5. Observations and Their Discussion.
6. Conclusions.

1. General Theory.

Suppose light of intensity i pass through a body of thickness x. Then the rate of change intensity is expressed by the simple formula $di = -kidx$, where i is the intensity at any point and k a constant of absorption depending only upon the wave-length. This gives us, for the intensity of the transmitted light the equation

$$i = i_0 \varepsilon^{-\kappa x}$$

where i_0 is the intensity of the incident light. If the absorbing body be a solution of strength c and length l, we may express x as a function of c and l, or the equation may be written

$$i = i_0 \varepsilon^{-\kappa c l}.$$

If the absorbing system has another component, its equations would likewise be

$$i_1 = i_0 \varepsilon^{-\kappa_1 c_1 l_1}.$$

Since the total transmission is the product of the separate transmissions, we have generally

$$i = i_0 \varepsilon^{-\Sigma \kappa_\lambda c l}. \tag{1}$$

This equation involves Beer's law,[1] which says that decreasing the concentration will have the same effect upon the transmitted light as decreasing the thickness, or when the product of concentration and thickness is maintained constant the absorption spectra will also

[1] Pogg. Ann., 86, p. 78.

be constant. The formula also says that for a system of n components represented by ΣAB the absorption will vary according to the exponential law so long as the components charge uniformily with the concentration. Probably very few experimenters, before the announcement of the dissociation theory, attributed deviations in the observed absorption to changes in the structure rather that to an untenable law.[1] However observations upon isotropic solids uniformly confirm the law. At present we may assume there is nothing wrong fundamentally with the formula, and that it gives us the means of testing the optical properties of solutions. If in our system ΣAB, two components A_1B_1 and A_2B_2 partly change so as to form new components A_1B_2 and A_2B_1 or if by dissociation ΣAB yields in part ΣA and ΣB, the solutions will show or will not show an apparent variation from Beer's law, according as a certain assumption which we may make is or is not true. If the absorption of a solution is an additive property of its elements, then the absorption of AB is the same as the absorption of $A + B$ and the absorption of $A_1B_1 + A_2B_2$ the same as $A_1B_2 + A_2B_1$ and there could be no change in the simple statement of Beer's law. This would simply mean that the absorption phenomena can give us no information in regard to changes in solution. For changes take place through elements already present in the solution and are not introduced from without. This view of absorption is stated by Gladstone as follows: "From the general rule that a particular base (say B)[2] or acid (say A) has the same effect on the rays of light with whatever it may be combined is aqueous solution, it may be inferred that when two bodies *combine*, each of which has a different effect on the rays of light, a solution of the salt itself will transmit only those rays not absorbed by either, or in other words transmitted by both. Thus if a red acid (A) and blue base (B) combine (AB), the resulting salt will certainly not be purple, but it may present some color intermediate between red and blue." This means that it is impossible to have any apparent deviation from Beer's simple law. If we change Gladstone's statement so as to

[1] A comprehensive review of the literature upon this point is given by Ewan, Phil. Mag. (4), 33, p. 317, 1892. Also in the British Association Reports for 1882 by Dr. Schuster.

[2] Parentheses and italics are the writers.

read do not combine but *coexist* in solution, his statement will then cover very dilute solutions, and his result would be expected. This is a result obtained by Ostwald,[1] who interprets Gladstone's results with this limitation. That there is apparent deviation from Beer's law by chemical reaction is too evident to the unaided eye to need detailed observation. In fact, upon these changes depends the much-employed method of titration. Now it may be questioned whether we have even a right to expect, *a priori* that AB would absorb the same as $A + B$. From dynamical considerations, we may regard the spectral region of absorption of A and B to correspond to the periods of their respective free vibrations. To absorb the same amount in the same spectral region in combination, implies that the product $A\,B$ is executing the vibrations of its original components, or in other words there is no bond of union between them. In general AB must have the characteristic vibration of an independent product, and characteristic absorption. This is not to say that the components do not determine the absorption of the molecule. For a combination in a particular way must affect the vibration in a particular way.

If a transparent radicle, one whose period of vibration lies outside of the visible spectrum, *combines* with a colored one, dynamically considered, such a system must execute a new vibration. Generally this will displace the absorption bands. The magnitude of the displacement would depend upon the relative importance of the radicles, and this importance at the outset can not be predicted. Observations show that the substitution of a heavier transparent radicle for a lighter transparent one in a colored molecule there is a displacement of the absorption toward the red.[2] The same thing

[1] Ostwald in Zeit. für Phys. Chem., 9, p. 579, examined the position of the bands for some 300 solutions by aid of the eye and by photography. He concludes that the spectra of dilute solutions of different salts with a common colored ion are identical. Referring to Gladstone's investigations, he says Gladstone's experiments seem to confirm this view.

[2] C. Kruss (Kalorimetrie und Quantitative Spectral Analyse, p. 156, 1891—book not available to the present writer) says that variation in the molecule by replacing H or other element by a radical varies the absorption in a definite sense.

Stenger (Wied. Ann., 33, p. 577), says that change in absorption is parallel to change in properties, *e. g.*, the absorption of rosalin is in the green and the substitution of methyl and phenyl for hydrogen displace the absorption toward the yellow and red respectively.

should happen in case of further addition of heavier radicles to the molecule or in the combination of molecules giving more complex molecules. Apparently the combination could displace the absorption so that it did not fall within the limits of the visible spectrum. In case of the coexistence of the components separately, *e. g.*, as ions, the observed absorption would arise from these components only, but the absorption in combination must not be confused with the absorption of such components. The displacement could begin suddenly when any sudden change in the grouping occurs. From dynamical considerations, therefore, color changes in solutions give us a means of testing the structure of solutions, and might in some cases reveal complex molecular aggregates [1] not suggested by other methods.

One method of attacking this problem consists in diluting the solution and increasing the length of the column so as to keep the amount of the solute in the path of light constant and then to observe if there is any shifting of the absorption bands.[2]

Such a difference could only arise from a difference between ΣAB and $\Sigma A + \Sigma B$. The more frequent method is to determine x for each concentration in the general formula. We have then, making c equal to unity,

$$x = -\frac{1}{l}\log_e \frac{l}{l_0}.$$

If i is measured as percentage of i_0, then

$$x = -\frac{1}{l}\log_e i$$

or if common logarithms are used x is the reciprocal of that length which will reduce the intensity of the transmitted light to one-tenth of its original value. The value of x so found throughout the spectrum divided by the concentration of the solution is a constant,

[1] B. Walter (Wied. Ann., 36, p. 523) says the width of the penumbra round an absorption band is closely connected with the presence of more complex molecular aggregates in solution.

[2] Lippisch (Sill. Journ. (3), 13, p. 304); Russel (Proc. Roy. Soc., 32, p. 258, 1881) found no parallelism between c and l, by this method; and Knoblauch (Wied. Ann., 43, p. 748) observed deviations.

$$\frac{\varkappa_1}{c_1} = \frac{\varkappa_2}{c_2} = \cdots = \frac{\varkappa_n}{c_n}.$$

This constant $\varkappa$ has been designated the extinction coefficient,[1] and on account of the convenience in calculating it, it has been extensively used by observers. In both these methods, the *general condition* would indicate a system of absorption curves intersecting each other. For it is clear that each component must have its own extinction coefficient, and on account of selective and overlapping absorption these coefficients not only change from wave-length to wave-length, but also some increase while others decrease. It is also possible, for example, in case of transparent ions to have two systems of absorption curves failing to touch each other at any point. It is further clear that the possibility of observing such a system of absorption spectra depends upon two things, viz: firstly upon a sufficiently sensitive optical system of measurement and secondly upon an appreciable magnitude for the extinction coefficients and an appreciable difference in those magnitudes. It may happen that an extinction coefficient is zero, *i. e.*, its corresponding component is transparent. It may happen that the coefficients are nearly equal. In the system AB yielding in part $A + B$, which occurs upon diluting water solutions, Gladstone's theory requires that the coefficient of the first should exactly equal the sum of the coefficients of the latter two components. The variation in the extinction coefficients is frequently not large, and sometimes within the limits of error of the observations. More generally the fault lies in the ability to command a sufficiently sensitive optical system.[2]

When solutions are studied spectrophotometrically it is not possible to test the optical laws completely and comprehensively in a few months. In the present paper the writer has had time to study but one solution. However, the solution was chosen with reference to its wide range of optical variation. The study of the optical behavior of solutions of ferric chloride was suggested to

[1] Bunsen & Roscoe, Pogg., Ann., 101, p. 242.

[2] The Vierordt double slit is the most sensitive arrangement previously used. It does not make use of the Lummer Brodhum principle of the vanishing line. It is further necessary to calibrate the slit, an error generally overlooked.

me by an article by Goodwin upon "The Hydrolysis of Ferric Chloride," studied electrolytically.[1] It was thought that the well-known color phenomena might be followed spectrophotometrically, that there might be a possibility of getting further information either to confirm or refute the hydrolytic theory; that the rate of formation of the final product could possibly be measured; and that some evidence relating to the above dynamical considerations could be obtained. That the presence of hydrolysis and dissociation would complicate the condition was apparent.[2] However, it was thought the phenomena could possibly be separated.[3] How well I have succeeded in this must be judged by the results.

2. Theory Applied to Experimental Conditions.

To study absorption experimentally it is desirable to isolate the components and study each separately. This we certainly can do in the case of isotropic solids, *e. g.*, glass plates. In dealing with solutions, the components in a few cases, *e. g.*, very dilute solutions, can be isolated. Just here, however, the great dilution makes quantitative measurements difficult. Seldom can the components be reduced to one and the phenomenon is necessarily complicated. Solutions must be placed in containing vessels, isotropic solids, which have absorption. Then if the absorption of the solute is desired, we have never less than three components—cell, solvent and solute—over which the summation sign in the general equation extends. Fortunately the cell and solvent may be eliminated. To do this there are several methods of procedure. We may, firstly, take measurements through the empty cell, and then through the cell

[1] Zeit. Phys. Chem., 21, p. 1, 1896. Another article continuing this investigation has appeared in the Physical Review, 11, p. 193, since the present experiments were completed.

[2] Knoblauch, l. c., says, "To test the Arrhenius law, solutions which hydrolize are to be excluded, since the color changes are produced not only by progressive dissociation, but by *chemical variation of the solution*." The italics are the authors and seem practically self evident. Knoblauch would probably accept the further qualification, hydrolizing solutions must be excluded from the test of the Arrhenius law unless measurements are made before hydrolysis begins.

[3] Antony and Giglio (Gazette Chemica, 25, 1, 1895) studied, colorimetrically, the intensity of the blue color, at the beginning and at the end of the colloid reaction, produced by addition of potassium ferrocyanide (quoted from Goodwin as all efforts to obtain this paper were fruitless).

filled with solution. Corrections according to the Fresnel theory for difference in refraction of glass, air and solution are necessary. Then the ratio of the light transmitted by solution and cell to the light transmitted by the cell alone, gives the light transmitted by the solution.[1] If the absorption of the solute is desired, this value must be divided by the absorption of the solvent. We may, secondly, pass light through a cell of thickness l_1, and then through another another cell of thickness l_2, containing end glasses of identical material. Then the ratio of the readings through the latter solution to those through the former solution give the absorption for a solution of thickness $l_2 - l_1$.[2] If the absorption of the solute is desired, we may proceed as before. This method requires no Fresnel correction. We may, thirdly, use two identical cells, fill one with water and another with solution. Then the ratio of the readings through the solution to the readings through the water give at once the absorption of the solute, when the solution is dilute. When the solution is not dilute two corrections are necessary. One correction due to the difference in the index of refraction of water and solution and another correction due to the fact that the solute displaces an appreciable part of the solvent, whose equivalent thickness is thereby reduced. In the study of the dilute solutions, the third method has been employed. In the study of the more concentrated but thin solutions, the third and second methods were used.

3. Theory Applied to Dilute Ferric Chloride Solutions.

When we come to apply the theory to the study of dilute solutions of ferric chloride, Goodwin's electrolytic investigations of this solution throw some light upon what may be expected. We have, according to Goodwin, at the outset α ions of $Fe^{\cdots}$ and 3 Cl', and β ions of $FeOH^{\cdot\cdot}$, $H^{\cdot}$ and 3 Cl'. At some instant, t, after dilution δ ions of $FeOH^{\cdot\cdot}$ have disappeared, forming with water colloid hydrate $(FeO_3H_3)_x$. We then have at any instant four components $FeCl_3$, $Fe^{\cdots}$, $FeOH^{\cdot\cdot}$, and $(FeO_3H_3)_x$ from which we might anticipate absorption. To the unaided eye the very dilute solution appears transparent. This would be prima facie evidence for regarding the

[1] Ewan, l. c., p. 327, illustrates the inconvenience of such processes.

[2] Hesse, Wied. Ann., II, p. 876.

components $Fe^{\cdots}$ and $FeOH^{\cdot\cdot}$ transparent. The apparent transparency of the dilute solutions also indicate there is too little of the original product $FeCl_3$ to give an appreciable absorption. (The experimental evidence indicates these components are not as near transparent as is desirable for convenient calculation.) Any color later would then arise from the $(FeO_3H_3)_x$ component and the amount of absorption would be proportional to its rate of formation. Formula (1) than becomes

$$i = i_0 \varepsilon^{-\kappa_\lambda c l}$$

where the concentration, c, is the only variable. If we take i_0 as unity and measure i in per cent., we have

$$c = -a \log_\epsilon i \tag{2}$$

where a is a constant and equals $\frac{1}{\kappa_\lambda l}$, and the cologarithms of the observed transmission are proportional to the product formed. If a solution of known concentration, n_1, is supposed to be A per cent., transformed we have $An_1 = -a \log_\epsilon i$, where a is the only unknown. If c is B per cent. of a solution of concentration n_2, we have

$$B = \frac{n_1 A}{n_2} \log \frac{i_2}{i_1}. \tag{3}$$

By sufficiently diluting the solution A can be made to approach 100 per cent. and hence B can be calculated with a fair degree of reliability, provided the solutions n_1 and n_2 are similar in composition and their ratio is not so large as to change the relation of the components. By the electrolytic method B can not be directly measured since the product is not an ion, however, it is formed at the expense of ions, and can therefore be approximated sufficiently well to indicate the general process. To repeat a little from Goodwin's article, if we designate the relative mobility of the $Fe^{\cdots}$, $H^{\cdot}$, $FeOH^{\cdot\cdot}$, and Cl' ions by u, u', u'', and v respectively, we have

$$\mu_{t=0} = \alpha(u + v) + \frac{\beta}{3}(2u'' + u' + 3v) \tag{4}$$

where $\mu_{t=0}$ is the molecular conductivity for infinite dilute solutions.

This formula of Goodwin we may extend to the colloid reaction when we have any instant t,

$$(5) \qquad \mu_t = a(u+v) + \frac{(\beta-\delta)2u'' + (\beta+2\delta)u' + 3\beta v}{3}.$$

If a decreased no farther during the formation of a colloid, (5) could be written in the form

$$(5a) \qquad \mu_t = \mu_{t=0} + \tfrac{2}{3}(u' - u'')\delta.$$

Then if β ions are entirely transformed into the colloid we have finally

$$(6) \qquad \mu_{t=\infty} = a(u+v) + \delta(u'+v)$$

unless the transformation involves further hydrolysis of the a ions and ultimate change of the entire product into FeOH and free ions of HCl. In which case we have

$$(7) \qquad \mu_{t=\infty} = u' + v.$$

The product, δ, in equations (5), (5a) and (6) corresponds to the product, B, in equation (3). Unfortunately the steps required to obtain δ, and the assumptions made, do not leave the value as accurate as desirable. In the first place, some of the mobility constants must be assumed; secondly the solutions are not infinitely dilute; thirdly we do not know that a remains constant as given in formula (5a) and (6); and fourthly the method which I have adopted to obtain μ from the equivalent conductivities is not free from error. We have a certain equivalent conductivity, $\varkappa$, before the colloid formation. This value will have a certain ratio to $\mu_{t=0}$ which we may express by the equation

$$\mu_{t=0} = m\varkappa$$

where m is a constant. We may further assume that this constant relation maintains during the colloid formation. If we then multiply the observed equivalent conductivities in Goodwin's tables by the value of this constant, m, we have values for μ_t during the process of the colloid formation. From these values of μ_t substituted in (5a) we may calculate δ for different intervals during the change.

4. USE OF THE APPARATUS AND ERRORS INVOLVED.

The spectrophotometric measurements were made with the Brace spectrophotometer.[1] The arrangement finally adopted was slightly different from the methods previously described. The light all comes from a single source. The light from one side of a broad thin acetylene flame falls upon one slit. The other side of the same flame falls upon the other slit, so that any fluctuation of the light would cause an equal fluctuation of the intensity before each slit.

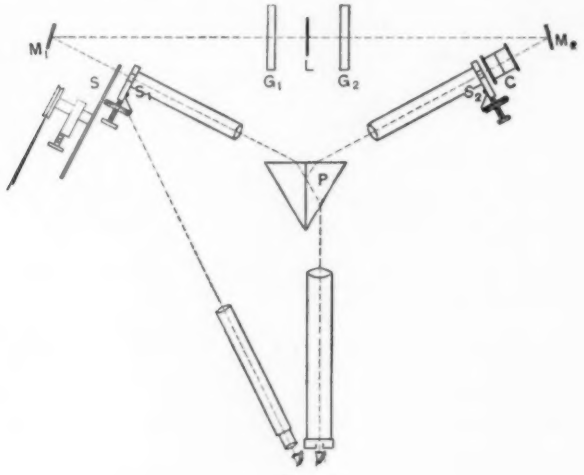


Fig. 1.

In Fig. 1, L is the light, G_1 and G_2 are ground-glass plates, M_1 and M_2 are reflecting mirrors, C is an absorption cell, S is a rotating sector, s_1 and s_2 are slits at the ends of the collimator tubes, P is the Brace prism, and T the observing telescope. Mr. Capps in using this instrument had placed the lights where the mirrors M_1 and M_2 are now located.[2] It is at once seen that any fluctuation in the intensity of one light would produce an error in the readings. Several sources of illumination were tried and none found to be as satisfactory as the incandescent light. However, the light from this source could not be made to cover the solid angle of the slit without the use of the ground-glass plates. This reduced the

[1] Phil. Mag. (5), 48, p. 420. Astrophysical Journal, 11, p. 1.
[2] Astrophysical Journal, 11, p. 29.

intensity of his field so much that it became difficult to take readings in the ends of the spectrum. Mr. Capps set about to make incandescent lights which would give large enough solid and uniform illumination to fill the solid angle of the field. After long and patient labor his mechanical ingenuity was rewarded with a satisfactory light. The present writer had neither time nor inclination to learn to make these lights. However, efforts were made to get different lamp factories to make them. Some companies would not furnish them in a small order and other companies forwarded lamps which did not fill the requirements. After wasting some months with these lights, acetylene was finally tried in the positions where the mirrors M_1 and M_2 are placed in the present figure. Obviously any lights burning in an open atmosphere will be subjected to some fluctuations, protected as much as possible. A trial showed that these lights would give all that was desirable in intensity. In fact the field was so bright that one could work with a slit as small as one tenth millimeter. These flames would also fill the field with exceptionally uniform light. Still there was a constant "pumping" amounting to at least one half per cent. The lights were then tried in the position used throughout the experiment. The light was placed in a position L without any ground glasses G_1 and G_2. To cover the entire field the broad side of three acetylene flames were turned together. The mirrors M_1 and M_2 were then adjusted so that corresponding parts of the flame appeared along the vanishing line of the field. Any fluctuating of the flame will now cause a variation in both parts of the field of view and will not interfere with the observations within narrow limits. The light then covers the entire field but not uniformly. To secure uniformity it was necessary to introduce the ground glasses G_1 and G_2. Unfortunately these glasses cut out 98 per cent. of the light which made readings difficult in the ends of the spectrum. Between $4750\,\lambda$ and $6500\,\lambda$ results could be obtained which are reliable to within one half per cent., at least so far as the optical measurements were concerned. Farther out in the violet the accuracy diminished rapidly. At $4250\,\lambda$ the vanishing line disappeared and it became necessary to match intensities as in many other photometers. By removing the ground-glass plates, this difficulty could be

somewhat overcome as far as 4000 λ. This, however, left the present light unsatisfactorily distributed in the field. Frequently sets of ten readings have been taken which showed a probable error no greater than one tenth per cent. Then with the plates G_1 and G_2 slightly shifted so as to change nothing but the variable slit readings another set of readings sometimes as accurate as the previous one could be obtained, but the mean result would often differ from the previous result by as much as three fourths of one per cent. This fact seems to indicate that outside the optical measurements personal errors arise. Possibly even in working with the vanishing line, personal judgments in regard to matching intensity are not entirely overcome.

The solution to be studied was placed in a cell, c, before the slit s_2. The slit s_1 was then adjusted until the line between the fields vanished, *i. e.*, until the fields matched. A sector, S, was also used as well as this slit s_1. By cutting out part of the light with the sector and making the final adjustment with the slit s_1, we can avoid the calibration of the slit, provided we use the sector in such a way as to keep the slit s_1 as near as possible to its original width. It is of course possible to avoid the use of the slit s_1 if we have an adjustable sector of the Lummer Brodhum type. In the present experiments I made use of an inexpensive sector cut into eight sections, used by Mr. Capps in his calibration of the slit.[1] By the use of the sector alone the difference between the two fields could be reduced to one sixteenth, and only this value need be compensated with the slit. Then with a one half millimeter slit, the error in observations arising from the slit can be reduced to one twentieth per cent. This value is certainly negligible in comparison to the errors of the results.

Two cells of the same thickness and having faces of the same kind of glass were used. One cell was used for water, the other for the solution. The water cell was first placed before the slit and readings taken. Then readings were taken through the solution cell and then again through the water to avoid any possibility of fluctuation due to a change in the intensity of the light. Except when studying velocity changes five readings were taken through

[1] Loc. cit.

the water, then ten through solutions and finally five through water. The ratio of the mean readings gives at once the per cent. of the original light transmitted by the solute. The only source of error in this method arose from the fact that the solution persisted in tarnishing the faces of the solution cell and only with the most scrupulous care in cleaning the cell could the absorption be made equal when the two were filled with water.

In the study of the time rate of change of solutions the position in the spectrum was not varied for several days. So that by keeping the ground glasses in the same position, and by keeping the burners clean, practically constant readings through water could be obtained. Readings through water could be taken just before the solution was prepared and then again later as a check when the rate of change in the solution would permit. Sometimes appreciable changes in the water readings occurred when it became necessary to stop the readings of the solution and prepare a new solution. In some solutions the changes were so rapid that only one reading could be taken, but a great number could be taken at short intervals. On account of these changes these solutions were studied for at least three samples for each concentration. Below .0012 normal these solutions show a variation for a given time during the first few minutes changes, as large as two per cent. The first few sets showed values much larger. It was thought that the light had an actinic action upon the solutions and that the difference arose from the length of time the light fell upon the cell. A simple test disproved this. It was known that a small change in temperature influenced the rate of change and a test showed that the trouble in part arose from this source. The solutions were prepared at 25° C. and maintained at that temperature in a constant temperature bath. This bath contained over one hundred and twenty liters of water, was double-walled, and wrapped with asbestos. With a temperature difference between the bath and the room of 5° C. the temperature of the bath would change about one degree in twelve hours, so that it was quite easy to regulate the bath by hand within .05° C. of the required temperature. No attempt was made to regulate the temperature of solutions while before the slit. At the outset some readings were taken and solutions returned to the stock. Although

the difference in temperature between the cell and the room during the summer months was very small, it was found that the trouble was at least in part here. Accordingly, the sample used before the slit was thrown away after a few minutes' use, and a fresh sample taken from the stock. This gave more uniform results, but not as uniform as the optical measurements would indicate one might expect. Just what the acting force or source of error may be is to me quite uncertain. Many of the solutions prepared identically, with absorption changes of the same relative magnitude, maintained at the same temperature during the experiment, and subjected only to the fluctuations of the bath after the experiment, were found to be quite different after six weeks. In some cases the more recently prepared solution of a given concentration had entirely precipitated the product and became as transparent as water, while the older solution showed its original color. Some of the stronger solutions (.0016 *n* and .0024 *n*) sometimes showed plainly a marked turbidity before the change had completely ended and at other times they did not. Though the latter solution would not reach the limit of transformation and sometimes began to precipitate at 25° C., a fresh solution heated, could be forced to change completely without any sign of turbidity. These facts lead me to believe that the solutions are very unstable, and that the errors do not arise from optical measurements and temperature changes alone.

5. OBSERVATIONS AND THEIR DISCUSSION.

The ferric chloride was prepared by sublimation. The solution was kindly tested by Mr. R. S. Hiltner and found to have .28 per cent. excess of iron. The concentration, mean of iron and chlorine, with respect to $FeCl_3$ was 3.0779 normal. While a solution prepared from resublimed ferric chloride which was purchased from a reliable firm, Mr. M. E. Hiltner found to have 1.7 per cent. excess of iron. All solutions studied were made from a sample of the former solution of one-tenth the concentration, namely, .30779 *n*. The concentrations of the solutions studied were .0003078 *n*, .0006156 *n*, .000821 *n*, .001026 *n*, .0012312 *n*, .0016416 *n* and .002462 *n* with reference to $FeCl_3$. However, in the tables, these concentrations are designated, for convenience, by their significant

figures. The absorption cell in which these solutions were placed was four centimeters long. A layer of the triple normal solution .0032 cm. in thickness contains the same amount of iron as the strongest of the above solutions. We could then for convenience designate both of these solutions by .0024 *n*. Their spectra would be identical if there is no change in the components of the system upon dilution. The thinner layer of the concentrated solution was placed between two plates of clear glass in the form of a wedge. This wedge could be driven at right angles to the slit to the position of desired thickness by means of a micrometer. This method of measuring thickness is certainly not as accurate as an optical method, but is certainly within the limits of the present measurements. These measurements were made upon the thin layer by the second and third methods described in the theory. The readings by the third method were used because the method obviated errors due to changes in intensity of the light. In the study of the diluted .0024 *n* it was however necessary to reprepare five solutions on account of time changes before a complete determination of its absorption spectra could be made, similar readings were made for .0008 *n* in the form of a film and .0008 *n* in dilution. For the latter the values are no more than a rough approximation of the transmission of a fresh prepared solution. The solution cannot be prepared, shaken, and a rough reading taken inside of one minute. During the next minute, in the violet one can see changes that amount to as great as 20 per cent. It was only possible therefore to make a setting, then to set the slit for a little larger transmission and to prepare a fresh solution. After about five trials one could find a setting which did not seem too small when a reading was taken as quickly as possible after the solution was prepared. Similar preparations were required for other points in the spectrum. The values obtained are not therefore the actual transparencies of this solution fresh prepared, but values which the transparencies possibly exceed by several per cent. in the blue. The transparencies certainly do not fall below these values and are therefore significant.

Table I. gives the values by this process for .0024 *n* and .0008 *n* in thin films and in fresh diluted solutions. Columns *a* and *a'* give

TABLE I.

λ	$n = .0024$		$n = .0008$	
	a	*b*	*a*	*b*
5750	99.3	100	100	100
5500	97.9	99.1	100	100
5250	95.8	97.9	99.1	100
5000	92.9	94.8	97.2	100
4750	87.4	90.9	95.7	98.9
4500	70	80.5	84.	94.3
4375	10.9	70.5	51.	90
4250		57.5		83.5
4125				
4000		23		61

transmissions for the films and dilute solutions respectively. It is of interest to compare these values with the transmissions of the same solutions after the colloid formation in Table II. The results are shown graphically in Fig. 5 where the same numbers correspond to the same amounts of ferric chloride before the slit and the letters *a*, *b*, *c*, correspond to concentrated, dilute, and colloid condition respectively. It is evident that diluting the solution makes it relatively more transparent. At 5000 λ the .0024 n in the concentrated form gives a transmission of 93 per cent. In the fresh diluted condition the transmission is 94.6 per cent. From Table X. of Goodwin's results we can infer the degree of ionization of this solution, and therefore also the amount of the original product present. If the ions were transparent this solution should show a transmission of 99.7 per cent. or an absorption of .3 per cent., whereas the absorption observed is 5.4 per cent. This leads to the inevitable conclusion that the ions are not transparent but that their absorption constant is smaller than the constant for the original product. The same conclusion is also drawn from the other concentration and from the other points in the spectrum. Goodwin's results indicate the presence of two positive ions for this dilution and it is apparent that we can not separate the absorption of these ions. However there are seven times as many of the $FeOH^{\cdot\cdot}$ ions as of the $Fe^{\cdot\cdot\cdot}$ ions, and it would seem reasonable to attribute a large part of the absorption to the larger product. Otherwise the

$Fe^{\cdot\cdot\cdot}$ ions would require a much larger coefficient of absorption than the original component. However, diluting the solution further apparently *decreases* the absorption of these ions more rapidly than the dilution. During such a process according to Goodwin, the relative amount of $FeOH^{\cdot\cdot}$ with respect to $Fe^{\cdot\cdot\cdot}$ is *increasing*. This would indicate greater relative absorption for the $Fe^{\cdot\cdot\cdot}$ ion. This action is the only evidence from the present observations to indicate the presence of both $Fe^{\cdot\cdot\cdot}$ and $FeOH^{\cdot\cdot}$ ions, but the observations are not conclusive upon this point.

Table II. contains a spectra study of the solutions after the colloid formation has practically ceased. Fig. 5 shows the results graphically. To obtain the calculated values it is assumed by exter-

TABLE II.

λ	n=.002462			n=.001231			n=.000821			n=.000615			n=.000308
	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.
7000	85.5			88.5			93.2			94.4			97.
6500	80.9	81.1	− .2	87.4	88.5	−1.1	91.6	92.3	− .7	93.8	94.1	− .3	97.
6000	73.1	72.7	+ .4	82.9	83.5	− .6	87.6	88.6	−1.0	90.8	91.3	− .5	95.5
5750	56.	56.1	− .1	73.3	72.1	+1.2	79.6	79.9	− .3	85.2	84.8	+ .4	92.
5500	37.	35.3	+1.8	54.8	55.3	− .5	65.9	67.2	−1.3	74.2	74.2	0	86.
5250	16.9	15.3	+1.6	34.2	34.6	− .3	47.8	49.	−1.2	57.8	58.5	−1.0	76.3
5000	5.2	5.2	0	19.2	19.2	0	32.5	32.5	0	42.4	43.2	− .8	65.5
4750				7.7	9.1	−1.4	18.3	20.9	−2.6	30.4	30.2	+ .2	55.2
4500							9.	13.3	−4.3	22.8	22.	+ .8	46.5

polation from Goodwin's Table X. that the .0003 n is 99.2 per cent. hydrolized at the outset. The assumption of 100 per cent. hydrolysis would not materially affect the calculation. The per cent. transmission of the colloid formation for other solutions is calculated for 5000 λ, since more observations were taken at this wavelength than in other parts of the spectrum. Formula (3) then becomes

$$B = -\frac{\log i}{618 n_2} \tag{3a}$$

and very similar expressions for other points in the spectrum. This gives for .0024 n, 86.7 per cent; for .0016 n, 90.6 per cent; for .0012 n, 98 per cent; and for .0008 n, 98.7 per cent; for .0006

n the value is assumed to be 99 per cent., which lies between the value for .0003 n and .0008 n. Now assuming these per cents. and taking the values of i_1 from .0003 n column, formula (3) can be used to determine i_2. This gives the calculated values recorded in Table II. In Fig. 5 the observed values are plotted in continuous lines and the calculated values in broken lines. These curves seem to agree as well as could possibly be expected except where the absorption is large in the blue and at 7000 λ. There is however a preponderance of negative differences in the difference columns. Table III.

TABLE III.

λ	n = .0024.	n=.0012.	n=.0008.	n=.0006.	n=.0003.
6500	86.5	110.	107.5	104.5	99.2
6000	84.8	100.4	107.	104.	99.2
5750	86.3	92.4	101.8	95.4	99.2
5500	81.7	98.9	102.7	98.7	99.2
5250	81.4	102.4	106.	105.	99.2
5000	86.7	98.7	98.7	100.5	99.2
4750		107.	106.3	99.4	99.2
4500			114.	92.8	99.2
Mean.	84.57				99.2

interprets the same readings in another way. Formula (3) is again used. A, in that formula, is again assumed to be 99.2 per cent. for .0003 n and the readings for this solution are assumed correct. From the observed intensities the per cents. of hydrolysis are calculated for the different concentrations. The variations here appear quite large although in the previous set of observations the differences appeared very natural. But these very differences account for this variation in per cent., since the observed differences are a larger per cent. of the low transmissions than they are of the high transmissions. These results also show that I might have obtained greater uniformity by taking some other solution for standard of reference.

Tables IV. and V. and Fig. 2 show the transmissions of the various solutions during the progress of the transformation. This study was made at 5000 λ, and has been repeated at least three times for each solution. The transmissions in Table IV. are taken to represent the transmissions of the colloid formation. For reasons given

TABLE IV.

Time.		n=.0003		n=.0006		n=.0008		n=.0010	
hr.	min.	Intens.	$-\log i$	I	$-\log i$	I	$-\log i$	I	$-\log i$
	2	92.0	.0362						
	4	85.5	.0680			95.6	.0195		
	5	82.2	.0851					95.	.0223
	7			87.2	.0595				
	8	80.0	.0969			90.8	.0419	93.	.0315
	12	77.6	.1101	81.2	.0904	87.0	.0605	90.0	.0458
	16	76.0	.1192			84.0	.0757	87.8	.0565
	20			76.7	.1152	80.2	.0958	85.0	.0706
	26	72.8	.1379						
	30					75.5	.1221	79.0	.1024
	40	69.8	.1561	68.8	.1624	71.7	.1445	74.5	.1278
1	00	67.5	.1701	63.6	.1965	65.0	.1871	68.0	.1675
1	20			60.2	.2204	60.4	.2190	62.5	.2041
1	40			57.2	.2426	57.2	.2426	58.0	.2366
2	00			55.0	.2596	54.8	.2612	54.6	.2628
2	40			51.0	.2924	50.2	.2992	49.3	.3072
4	00			48.0	.3188	45.0	.3468	43.7	.3595
6	00					40.5	.3925	38.7	.4123
6	40			46.8	.3298				
8	00					37.8	.4225	35.7	.4473
19 days		65.5	.1838						
16 "	2 hours			42.4	.3726				
18 "						32.5	.4881		
8 "	3 "							25.	.6021

in discussing Table I., the transmissions of the stronger solutions need some correction before they can be taken to represent the formation of a colloid hydrate. Evidently when i_1 and i_2 are the transmissions of components A and B respectively, and i the transmissions of the two, $i = i_1 i_2$. At the outset we have no colloid or $i = i_1$. Then the observed transparency at the outset divided into the transparency at any other instant would give the transparency of a new product, provided, the original product remains constant. However the colloid forms at the expense of the other product. We may then assume that the absorption of this product decreases at the same rate the other forms. Then by successive approximations, we may obtain the transmission of a colloid alone. We observe, *e. g.*, i_1, at the outset, and later i, and $i_2 = i/i_1$, for the first approximation. Then $(100 - i_1)\, i_2$ is the approximate absorption

of the original product remaining. Then $100 - (100 - i_1)\, i_2$ would be the corrected value for i_1, which divided into i gives the second approximation for i_2. Further approximation is scarcely necessary.

As noted in discussion, Table I., the absorption at the outset may arise from both the iron ions rather than from one and a small per cent., never greater than .3 per cent., may arise from the original product. In this change one of these products, the Fe-OH ion is certainly active and if the other components are active it will make but a trifle difference, and scarcely affect the values obtained by the second approximation. In fact so far as the general course of the formation of the final product is concerned, it is not necessary to assume here any intermediate ion whatsoever. In Tables IV. and V. are also tabulated cologarithms of the colloid transmission. From formula (1) it is evident that these values are proportional to the

TABLE V.

A = Observed transmission. B = Transmission calculated for the hydrolized product.

Time.		n=.0012.			n=.0016.			n=.0024.		
hr.	min.	*A.*	*B.*	$-\log i$.	*A.*	*B.*	$-\log i$.	*A.*	*B.*	$-\log i$.
	2	97.	99.5	.0022	95.7	99.9	.0004	94.6	100.	.0000
	4	96.5	99.	.0044	95.3	99.5	.0022	94.5	99.9	.0004
	8	94.8	97.3	.0119	94.8	99.	.0044	94.3	99.7	.0013
	12				94.1	98.3	.0074			
	14	92.2	94.3	.0255						
	20	89.8	91.9	.0367	93.1	97.2	.0123	94.	99.4	.0026
	30	84.8	86.5	.0630	91.2	95.2	.0214			
	40	80.	81.6	.0883	89.7	92.5	.0339	93.	98.3	.0073
1		71.	77.2	.1415	84.8	88.4	.0535	91.8	97.2	.0123
1	20	64.5	65.5	.1838	78.2	81.4	.0894	89.5	94.5	.0246
1	40	59.1	60.0	.2218	70.8	73.4	.1343	86.5	91.4	.0391
2		54.9	55.6	.2549	63.8	66.	.1805	81.9	85.7	.0670
2	40	48.3	48.9	.3107	57.	52.5	.2798	71.8	74.2	.1296
3					46.	47.4	.3242	66.8	69.	.1612
3	20				43.	44.4	.3526	61.	62.8	.2020
3	40				40.5	41.7	.3788	56.2	58.1	.2358
4		40.4	40.8	.3893	39.	40.2	.3958			
6		34.9	35.1	.4546	31.4	32.3	.4908	34.8	35.1	.4547
8		31.	31.2	.5058	26.7	27.5	.5607	26.2	26.3	.5800
10		26.6	26.7	.5735	24.9	25.7	.5901	21.2	21.3	.6716
14	days.	19.1	19.2	.7167						
22	"				12.5	12.7	.8962			
32	"							5.2	5.2	1.2840

total amount of the product formed. Therefore these values have been plotted here directly and are found in Fig. 3. By dividing

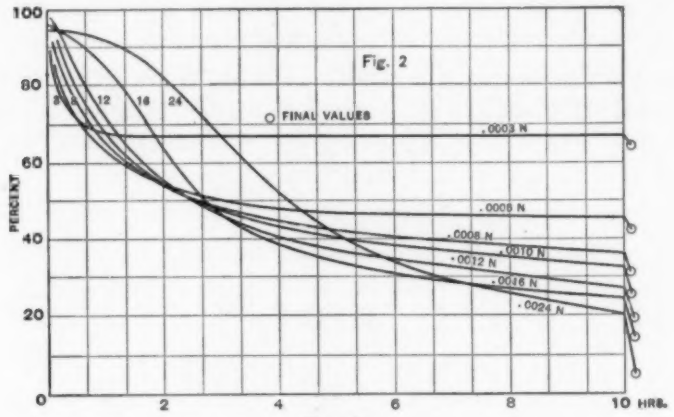


Fig. 2.

these values by the thickness of the cell 4 cm., we obtain the extinction coefficient, the latter divided by the concentration gives the absorption ratio. However these values give no additional infor-

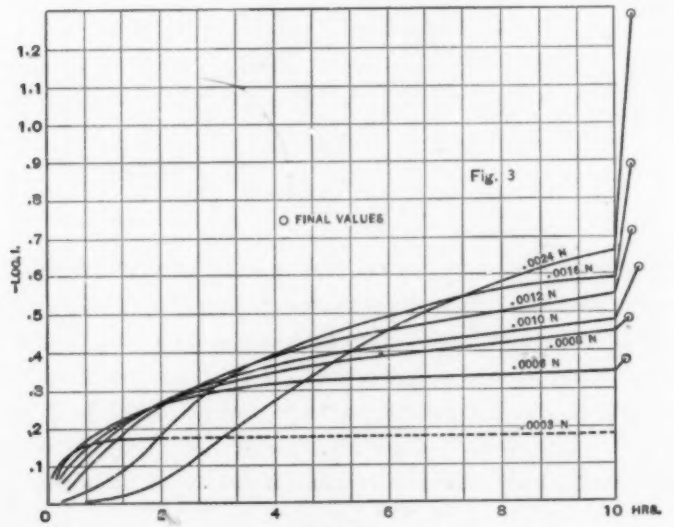


Fig. 3.

mation upon the rate of formation. Again the final values of cologarithms i in the .0003 n are taken to represent 99.2 per cent.

transformation and by aid of formula (2) the per cents. transformed for all other values of cologarithms i, both for .0003 n and other concentrations are calculated. The values of δ are calculated, as indicated in the theory, from Goodwin's data by use of formulæ (5) and (5a). The values so obtained for δ and B are given in Table (VI.) under the names of Goodwin and Moore. The concentrations

TABLE VI.

G = Goodwin. M = Moore.

Time.	n=.00303		n=.000606		n=.000802		n=.001211		n=.0016	n=.002422	
hrs. min.	G.	M.	G.	M.	G.	M.	G.	M.	M.	G.	M.
1	3.	10.	0.		0.	3.9					
4	24.6	36.7	.3					.6	.22		
10	44.2	56.	2.0	20.8	1.3	10.3		2.2	.6		
20	59.7	68.4	9.	31.1		19.4	.04	5.	1.24		.18
35	70.5	80.8			10.1	27.			2.85	.6	
45			30.5	45.8	21.3		4.2	13.7		1.0	
1 00		91.9	39.	53.		37.8	7.8	19.1	5.4		.83
1 15	84.3										
1 30			52.	61.8	38.4	46.7	18.3	27.4	11.3	2.4	2.37
2 00				70.	46.4	52.8	26.3	34.4	18.3	5.9	4.53
2 30			63.1				32.2	39.4	25.8	9.1	7.63
3 00			66.9	80.8	56.6		37.8		32.6	13.5	10.9
3 30							41 7		37.	17.6	14.8
4 00	94.3			86.	62.8	71.8	45.	52.5	40.	21.5	
5 00			74.		65.		50.2			30.3	
6 00						79.4	55.	61.3	56.6[1]		30.7
									59.6[2]		
Final	103.6	99.2	104.	100.5	98.	98.7	103.	97.9	90.6	80.4	86.7

are according to Goodwin. The values are shown graphically in Fig. 4. This system of curves shows the same general character and indicates approximately the same final condition. The wide gap between the curves at some points I can hardly attribute to the errors in the data of either observer or to the method of calculation. There is a marked tendency, except for the .0024 n, for the writer's solutions to begin the reaction sooner than Goodwin's solutions. They behave as if they were warmer. However, I rather anticipate a difference in the solutions, possibly due to a difference in internal condition rather than due to a concentration difference.

[1] 8 hrs. [2] 10 hrs.

The observed concentration difference of 1.7 per cent. would cause a difference of opposite kind.

It is desirable also to follow these transformations at other points in the spectra. Other wave-lengths will not be so favorable as this one since we can in this position begin with large transmissions, obtain large absorption for small changes and finally large absorption when the product is entirely formed. However, some tests were made at 6000 λ where the absorption seems to form a penumbra. If the absorption at the two points arises from the same molecules, the extinction coefficients should be in a constant ratio to each other. This seems to be true for the final products in Table II.

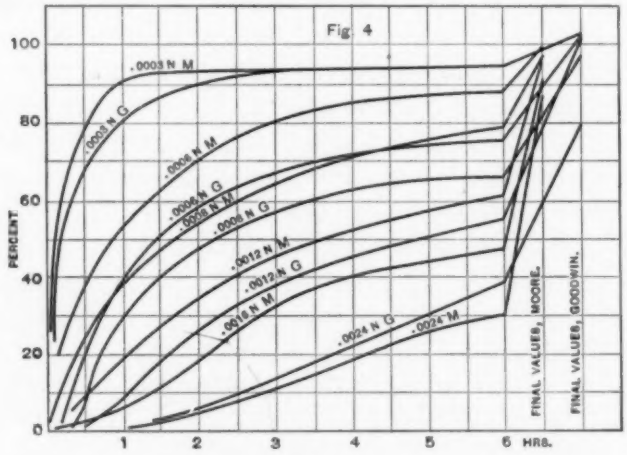


Fig. 4.

The extinction coefficients were so small, however, for the more dilute solutions that the observations, though giving a slight curve could have nearly coincided with previous curves by magnifying them or could have approached a straight line and in either case have been within the limits of error of the observations. It was thought more might be accomplished with the .0024 normal. I tried four solutions of this concentration. The transmissions of these solutions when plotted spread over a field 1.5 per cent. wide. In the early part of the reaction the total absorption after the transformation is practically ended, is only 26.9 per cent. So that a difference of 1.5 per cent. in the early readings makes consider-

able error in the rate of formation. These readings indicate transformations 10 per cent. larger for .0024 *n* after one and two hours change than at 5000 λ. Plotted as a curve in Fig. 4 they would cross the .0024 *n* curve between 4.5 and 6 hours, but ultimately reach as high a value. If the colloid molecules $(FeO_3H_3)_x$, were not all alike, but if, for some molecules x had one value, and for other molecules another value; and if one set were formed early, in the transformation and another set later, just such action as here observed would take place. Antony and Giglio[1] assumed the presence of $FeCl_2(OH)$ and $FeCl(OH)_2$ in varying proportion depending upon the dilution. Now if we modify this statement and say one product appears early and another later, the selected absorption of the assumed products would produce the observed optical phenomena. Since, however, the final curves show at all points absorption in proportion to the concentrations, it is evident that the ratio of the possible different components is finally the same for all concentrations. The absorption spectra observed could, of course, arise from products of the form $FeCl(OH)_2$. However, from the present standpoint of the theory of solutions and the observations of Goodwin the product $(FeO_3H_3)_x$ may be regarded as practically demonstrated if the final product in solution is FeO_3H_3 we could prepare this solution independent of $FeCl_3$ and test it for identical absorption spectra.[2] The writer may make such an examination later.

In Fig. 5 we find the thin films of a triple normal solution represented .0024 *n* and .0008 *n* to have large absorption bands beginning very suddenly and falling nearly perpendicularly. These absorption bands recede toward the violet when the film is made thinner. From the sharply defined character of the absorption it appears that the molecules have an equally well-defined period of vibration and probably are quite uniform in structure. The presence of well-defined anomalous dispersion in this solution is at once suggested. However, for the colloid formation, the range of molecular vibration is not so uniform. The umbra shades off slowly

[1] Antony & Giglio (reference Zeit. Phys. Chem., 19, p. 191).

[2] Goodwin's recent paper (PHYS. REV., 11, p. 193) makes a very similar test, viz.: The accelerating effect of FeOH upon the hydrolizing process.

into a penumbra. Hence again the suggestion of less regularity in the structure of this product. The final curves for the colloid (Fig. 5) are, as previously shown, proportional to the product at all

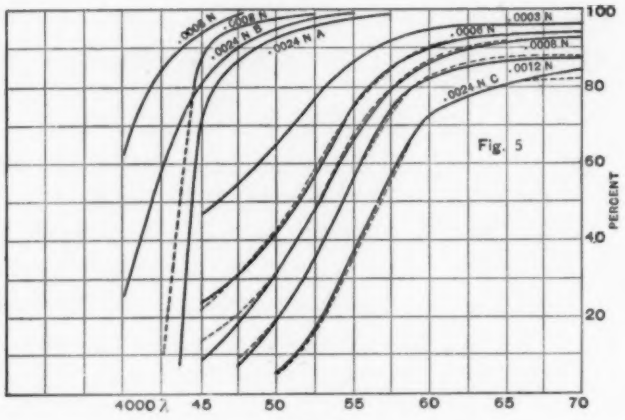


Fig. 5.

points. This shows that for final examination any mixed red or yellow light could be used in the study instead of spectral lines or the color could be compared with another absorption red.

6. Conclusions.

1. A study of the absorption spectra has proved to be a good method for following the progressive changes in the colloid formation, and will be serviceable whenever any color changes take place.

2. The presence of ionization is detected and the fact that the ions are not completely transparent is shown.

3. A quantitative determination of the rate of ionization is impossible in the present case, but it is indicated that it is quite possible with some solutions.

4. There is but slight direct evidence for the presence of two iron ions so clearly shown by the electrical method. However, the general agreement of the optical with the electrical methods of finding the rate of formation of the final products gives us further, through indirect, reason for accepting Goodwin's theory of the reaction.

5. There is some, but rather slight, evidence for thinking that the molecules of the final product are not all of the same magni-

tude, *i. e.*, x in the formula $(FeO_3H_3)_x$ may have more than one value for different molecules.

6. The clearing of the solution and the displacement of the absorption bands toward the violet upon dilution; and the subsequent formation of a much greater absorption band displaced toward the red upon the formation of a more complex molecule, confirm the dynamical considerations.

7. *General Conclusion.*—The optical study of absorption spectra on account of both the optical theory of the relation of absorption to dispersion and the relation of absorption to the molecular structure of solutions should be more general. The method is not as easy to manipulate as the raising of the boiling point, lowering of the freezing point, osmotic pressure or electrical methods; and by reason of the transparency and general overlapping of the absorption spectra has nowhere near their range of application. However, there is a possibility that the method will show complexity of structure in some cases not brought out by other methods. Further confirmation of results by the other methods is also desirable.

UNIVERSITY OF NEBRASKA, January, 1901.

COHERERS SUITABLE FOR WIRELESS TELEGRAPHY.

By Carl Kinsley.

IT is my purpose to show that however much uncertainty attends the use of the wireless telegraph it need not be due to the coherers. It has often been pointed out by the promoters of wireless telegraph companies that the coherers may be relied on in practice. Unfortunately, the scientific experimenter, while presumably impartial, has found coherers unsuited to his purpose, and so by his voluminous writings, has created a popular distrust of an essential part of the wireless telegraph apparatus.

Methods of determining the sensitiveness of coherers have not been used which will enable either the impartial investigators or the practical operators to compare results. I will therefore give in detail the method I have found the most satisfactory in practice in the hope that other experimenters may employ the same or a better one which will enable us to interpret each others results.

For the purposes of wireless telegraphy the most sensitive coherer is the one which, with unchanged conditions at the transmitting station, will receive the signals when its own aërial wire is the shortest. Arrange the apparatus, for the sake of simplicity, so that at the receiving station an insulated aërial wire is attached to one terminal of the coherer while the other terminal is connected to a ground wire. A bypath should be furnished—usually by the local circuit of the recording apparatus—with large self-induction so as to eliminate possible static atmospheric charges. The relative sensitiveness of coherers may be obtained by comparing the length of aërial wire which will always cause the coherer's resistance to fall when the signals are received, with the length necessary for a standard coherer.

The following laboratory method invariably gives the same relative values and it may be called the direct potential difference method of testing. If a coherer has a p. d. between its terminals

when its resistance is high—practically infinite—its resistance will be unchanged as the potential is raised until a certain value is reached, when the resistance will suddenly fall. The more sensitive the coherer, the smaller is the p. d. necessary to produce this sudden change in its resistance. This method of rating the sensitiveness of coherers is extremely important, as it may always be used with certainty, and is in no way dependent on the condition of a standard coherer, or of an uncertain transmitting apparatus. Two experimenters[1] seem to have appreciated this characteristic of coherers, but one draws his conclusions from the action of one coherer, and the other merely gives his conclusions without experimental conditions or data.

Many others[2] fail to determine the initial condition of the metals used, and consequently make quantitative results impossible.

The requirements for a satisfactory coherer for wireless telegraphy are few but most important. The coherer must be uniform in its action. Its sensitiveness must be great and must vary but little from time to time. The final resistance of the coherer must fall below some predetermined value after each signal, but it need not be low, as the relay can be adjusted for any value desired.

The performance of particular coherers will illustrate the methods of testing and show how nearly the preceding conditions are complied with in coherers which have been used with entire success for automatic wireless telegraphy. The testing signals were sent at two and one half second intervals. The resistance of the coherer was obtained by calibrating the readings of a very sensitive Weston voltmeter which was connected in series with inductive resistance, the coherer and a source of constant E.M.F. The measuring current was always less than 0.001 ampère.

A coherer may be made so that its final resistance is either dependent or nearly independent of the height of the aërial wire, and consequently of the energy utilized by the receiver. With the transmitter seven miles from the receiver—in New York harbor at stations equipped by the Signal Corps U. S. A.—coherer No. 1, for

[1] Trowbridge, Am. Jour. of Sci., September, 1899. Blondel et Dobkevitsch, Compt. Rend., April 23, 1900.

[2] J. C. Bose, Proc. Royal Soc., July 21, 1899. T. Mizuno, Phil. Mag., November, 1900.

instance, showed the following values as the results of about 300 observations:

COHERER No. 1.

Final resistance = 166 ohms when 150 ft. of aërial wire were used.
" " = 345 " " 100 " " " " " " "
" " = 834 " " 75 " " " " " " "

Coherer No. 2, however, gave a uniformly low resistance as long as it was affected at all by the electrical waves.

COHERER No. 2.

Final resistance = 18 ohms when 150 ft. of aërial wire were used,
" " = 26 " " 100 " " " " " " "
" " = 30 " " 75 " " " " " " "

A further slight decrease in the length of the aërial wire caused an entire discontinuation of the signals.

The above coherers were of the same sensitiveness, since each required the same length of aërial wire to effect a change in their normally high resistance. Coherers such as No. 1 can conveniently be used for testing purposes on account of their interesting property of a final resistance depending on the height of the aërial wire. In San Francisco harbor, for instance, where the transmitter was only about two miles from the receiver—between two wireless telegraph signal stations of the Signal Corps of the U. S. A.—the following resistances were observed when Coherer No. 1 was used.

Final resistance = less than 10 ohms when 75 ft. of aërial wire were used with the coherer.

Final resistance = less than 10 ohms when 70 ft. of a. w. were used,
" " = " " 10 " " 55 " " " " " "
" " = 33 45 " " " " " "
" " = 184 35 " " " " " "

The coherer was not affected when 25 feet of aërial wire were used.

If it ever becomes necessary to signal with only 25 feet of aërial wire a coherer more sensitive than the preceding one must be employed. For practical reasons it was not desirable to use a coherer more sensitive than No. 1, and so a wire at least 35 feet long was used. A page of data will give an idea of the variations found in

some practical coherers which are entirely satisfactory for wireless telegraphy.

COHERER No. 1.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

1.8	2.2	1.7	1.8	2.0	2.4	2.1	2.4
2.2	2.2	2.1	2.6	2.0	2.6	2.6	2.0
2.5	2.5	2.5	1.5	1.7	2.1	1.8	2.1
						Average =	2.1

Final resistance after the signal was received:

260	390	570	150	390	230	200	150
200	150	150	110	130	150	390	150
390	150	200	260	150	390	150	150
						Average =	234

Again:

260	200	150	260	260	320	110	390
150	200	150	390	200	320	260	200
200	150	200	70	390	260	70	260
						Average =	226

COHERER No. 3.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

2.4	3.0	3.0	2.2	2.2	2.6	2.8	2.4
3.1	2.6	2.5	2.0	2.5	2.5	2.5	2.0
3.4	2.5	2.5	2.2	1.8	3.0	2.5	2.8
						Average =	2.5

Final resistance after the signal was received:

260	150	230	260	320	200	200	260
150	200	150	320	150	230	130	150
200	260	200	390	230	180	230	260
						Average =	230

Again:

290	200	200	260	110	260	200	
260	260	260	260	200	390	150	
150	390	230	530	260	320	260	
						Average =	259

COHERER No. 4.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

5.0	2.6	5.0	4.0	7.0	8.0	5.0	4.0
8.0	5.0	6.0	5.6	6.5	8.0	4.0	4.6
5.2	6.0	5.5	5.6	6.6	6.2	5.0	5.0

Average = 5.5

Final resistance after the signal was received :

70	55	80	70	35	70	130	150
10	15	(*a*)	260	70	10	55	70
150	10	95	55	70	70	70	55

Average = 72

(*a*) The coherer did not break down when the signal came. When tested it was found that 8 v. p. d. were required, showing an insensitive condition. It has thus been found that if a coherer is used which will not break down under 8 v. p. d., it will never be affected by the signals received by that length of aërial wire. Sometimes an increase of two or three feet in fifty is sufficient to put a coherer which was not affected, into operation.

Coherer No. 5.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down :

4.0	4.0	3.8	4.2	3.4	4.0	4.5
3.3	4.2	4.4	4.0	2.6	4.0	3.5
3.0	3.4	4.0	4.0	4.5	4.0	3.8

Average = 3.8

Final resistance after the signal was received :

700	870	700	570	700	800	1300	320
1005	700	530	870	570	530	570	870
700	700	530	390	1005	870	1300	700

Average = 746

Upon testing the coherers it was always found that as the aërial wire was shortened, the coherers ceased to act always in the order of their sensitiveness. In the case of the above coherers the order was No. 4, No. 5, No. 3 and closely following it No. 1. All of them may be used for receiving wireless telegraph messages automatically, but it will be readily seen that the adjustment of the apparatus when No. 4 is used must be different from the adjustment with No. 5 on account of the difference in their final resistance. If the potential at which the coherer breaks down varies widely, the coherer cannot be used satisfactorily under any circumstances.

The active material of coherers is composed of metal filings. I have refrained from giving the composition of the filings used in the above coherers as I wish to emphasize most strongly the fact that the sensitiveness does not depend on the metal or metals employed. Coherers of any degree of sensitiveness desired may be made of any metal. It is only necessary to treat each metal in accordance with its peculiar nature. In general it may be said that the more readily the metal oxidizes the more carefully must it be manipulated. It is not sufficient to treat every metal in the same way and then from the performance of the coherers to draw up tables of the relative sensitiveness of the metals. It has thus been decided, for instance, that lead filings are too insensitive to be used for coherers. The following coherer illustrates the point. In an atmosphere of CO_2 the lead was filed and placed in the tube which was then sealed, without bringing the filings into contact with the air.

COHERER No. 6.

Sensitiveness as shown by the p. d. in volts at which the coherer breaks down.

0.8	1.0	1.0	1.2	1.1	0.8	1.3	1.4	1.2	1.3
1.1	1.0	1.2	1.2	1.0	0.9	1.2	1.0	1.3	1.3
0.7	1.0	1.2	1.0	1.0	0.9	1.1	1.4	1.1	1.4

Average = 1.1

Nickel is a very satisfactory metal to use, as it can be handled in the open air and can easily be made to give any sensitiveness and ultimate resistance desired for wireless telegraph work. As a final illustration, the test of the sensitiveness of a non-adjustable, exhausted coherer filled with pure nickel filings, and having an ultimate resistance of three hundred ohms is given below.

COHERER No. 7.

Sensitiveness as shown by the p. d. in volts at which the coherer breaks down.

2.4	2.4	2.0	2.2	1.8	1.8	2.1
1.7	2.6	2.4	2.8	2.2	2.4	2.1
1.4	2.0	2.0	2.0	1.8	2.2	2.0

Average = 2.1

This coherer was designed to give a resistance of three hundred ohms after the signals were received, as that was found to be the

best value to use with the relays that were employed. This coherer and similar ones have been used with perfect results in practical wireless telegraphy with automatic recorders.

The limit of the sensitiveness of coherers for wireless telegraph work is defined by the p. d. which must always be present between the terminals of the coherer whenever a relay is used. This p. d. should always be kept as low as possible to preserve a safe working margin and thus to prevent any local disturbance from combining with this constant p. d. to produce a temporary p. d. which is high enough to break down the coherer, thereby producing a false signal. It may be of interest to know that the local p. d. I have found best to use is 0.4 volt. As the current must also be kept small—say less than 0.002 ampère—it is obvious that a very sensitive relay must be used. Indeed, it has been found that a relay which will be operated by a current of 0.001 ampère is the most satisfactory.

A GRAPHICAL METHOD FOR ANALYZING DISTORTED ALTERNATING CURRENT WAVES.

BY A. S. LANGSDORF.

THE problem of resolving a distorted wave into its fundamental and harmonics is one which frequently arises in alternating current working, so that a simple solution is of practical interest. The analytical solution, based on Fourier's series, is of course well known, and a number of graphical and mechanical methods more or less dependent upon it have been proposed from time to time.[1] The principal objection to their use is that in some of them several auxiliary irregular curves must be constructed, while in others a planimeter or other integrating device must be at hand. The method described below merely requires the construction of circles and straight lines.

Nearly all of the curves met with in alternating current practice contain only the odd harmonics, so that the wave can be represented by the equation

$$e = a_1 \sin \omega t + a_3 \sin 3\omega t + a_5 \sin 5\omega t + \cdots$$
$$+ b_1 \cos \omega t + b_3 \cos 3\omega t + b_5 \cos 5\omega t + \cdots$$

where $a_1, a_3, \cdots b_1, b_3 \cdots$ are functions of the amplitudes and phase positions of the component sine curves. The complete analysis of the distorted wave requires the determination of these constants. The analytical method is as follows :[2]

[1] London Elec., Jan. 22–29, 1892, Harmonic Analysis, J. A. Fleming.
London Elec., Feb. 5, 1892, Harmonic Analysis, John Perry.
London Electrician, June 28, 1895, Periodic Functions Developed in Fourier Series, The Graphical Method, John Perry.
Ecl. Electrique, 15, 1898, Harmonic Analysis, S. Berson.
Elec. World, Vol. 31, 1898, Harmonic Analysis, Houston and Kennelly.
Proc. Royal Soc., Vol. XXVII, 1878, p. 371, Sir William Thomson.
Proc. Phys. Soc., Professor Henrici.
Am. Jour. Sc., 5, 1898, Harmonic Analyzer, A. A. Michelson and S. W. Stratton.

[2] Alternating Currents and Alternating Current Machinery, p. 695. D. C. and J. P. Jackson.

Divide the base of one loop of the curve into $(n + 1)$ equal parts, so that the angle equivalent to the linear distance between any two

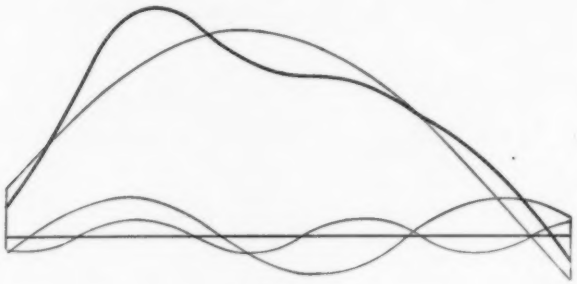


Fig. 1.

points of division will be $\frac{180^\circ}{n+1}$. The ordinate at the (x)-th point of division will then be

$$e_k = a_1 \sin \frac{k180}{n+1} + a_3 \sin 3\frac{k180}{n+1} + \cdots + b_1 \cos \frac{k180}{n+1} + b_3 \cos 3\frac{k180}{n+1} + \cdots.$$

If similar equations are formed for the ordinates at each point of division, there result n equations of the first degree, by means of which the constants, $a_1, a_3, \cdots, b_1, b_3, \cdots$, to n terms can be determined. The general solution for any pair of coefficients, such as a_m and b_m, takes the form

$$\text{(I)} \quad a_m = \frac{2}{n+1}\left[e_1 \sin\left(m\frac{180}{n+1}\right) + e_2 \sin\left(2m\frac{180}{n+1}\right) + \cdots + e_k \sin\left(km\frac{180}{n+1}\right) + \cdots + e_n \sin\left(nm\frac{180}{n+1}\right)\right],$$

$$\text{(II)} \quad b_m = \frac{2}{n+1}\left[e_1 \cos\left(m\frac{180}{n+1}\right) + e_2 \cos\left(2m\frac{180}{n+1}\right) + \cdots + e_k \cos\left(km\frac{180}{n+1}\right) + \cdots + e_n \cos\left(nm\frac{180}{n+1}\right)\right].$$

The significance of these equations from the graphical standpoint can be seen by referring to Fig. 2, which represents in polar co-

ordinates the curve of Fig. 1. Here the original $(n+1)$ equal linear divisions are replaced by the $(n+1)$ equal angular divisions, while the quantities e_1, e_2, etc., are represented by the successive radii vectores.

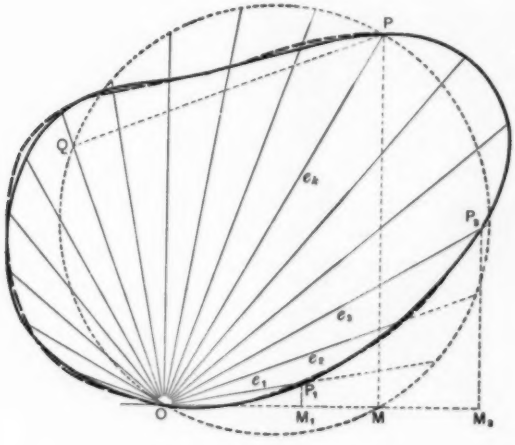


Fig. 2.

Let OP represent the vector e_k; $\angle POX$ will then be $k \cdot \frac{180}{n+1}$; consequently we have

$$PM = e_k \sin\left(k\frac{180}{n+1}\right) \quad \text{and} \quad OM = e_k \cos\left(k\frac{180}{n+1}\right).$$

But these expressions enter into equations I. and II. for the special case in which $m = 1$; therefore if we scale off P_1M_1, P_2M_2, $\cdots$ OM_1, OM_2, $\cdots$ etc., we shall have

$$a_1 = \frac{2}{n+1}(P_1M_1 + P_2M_2 + \cdots) = \frac{2}{n+1}\Sigma PM$$

and

$$b_1 = \frac{2}{n+1}(OM_1 + OM_2 + \cdots) = \frac{2}{n+1}\Sigma OM.$$

Due attention must be paid to the sign of OM.

Inspection of I. and II. shows that the constants corresponding to higher harmonics involve angles which are simple multiples of those used in finding a_1 and b_1. If a circle is constructed on e_k

as a diameter (Fig. 2), the successive radii vectores will intersect its circumference in points such as Q, so that

$$PQ = e_k \sin POQ \quad \text{and} \quad OQ = e_k \cos POQ;$$

if now $\angle POQ$ is made equal to $km \frac{180}{n+1}$, PQ and OQ will correspond to terms in I. and II., respectively; hence,

$$a_m = \frac{2}{n+1} \Sigma PQ \quad \text{and} \quad b_m = \frac{2}{n+1} \Sigma OQ.$$

In order to make $\angle POQ = km \frac{180}{n+1}$, it is only necessary to find a point of intersection on the circumference, which is km divisions from P.

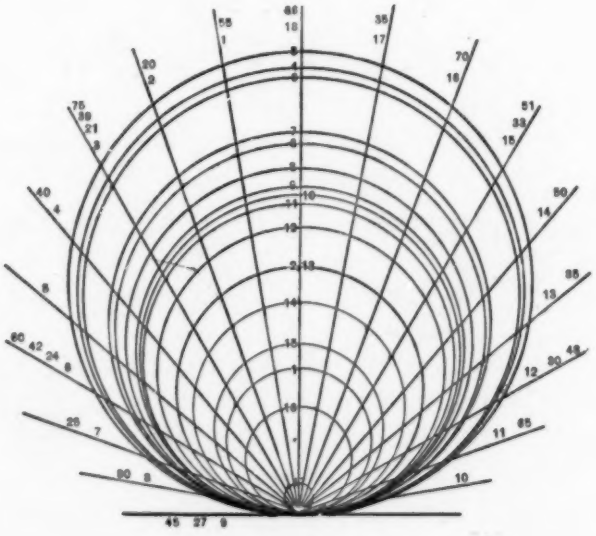


Fig. 3.

In obtaining the summations ΣPQ and ΣOQ it is necessary to pay strict attention to the signs of the constituents. The criteria for the signs of PQ and OQ are as follows:

PQ is *positive* if Q is reached by passing through P an *even* number of times in the counting process; it is *negative* if the number of passages through P is *odd*.

OQ is *positive* if the number of passages through Q is *even*; and it is *negative* if the number is *odd*.

If a circle were to be constructed on each vector in Fig. 2 in order to carry out the above method, the figure would become too complicated for rapid work; this difficulty can be avoided by plotting all the vectorial quantities along a common axis, as in Fig. 3; the circles in this case do not intersect each other.

The following method will be found well adapted for quickly scaling off the required quantities with minimum chance of error.

Number the circles corresponding to e_1, e_2, e_3, etc., 1, 2, 3, etc., respectively; and mark the successive radii vectores $_1$, $_2$, $_3$, etc. (Fig. 3.) Designate the intersection of circle p with vector r by the symbol (p, r); and let $O(p, r)$ represent the distance from this intersection to O, while $p(p, r)$ represents its distance from the vertex of the circle p.

We then have

$$a_1 = \frac{2}{n+1}\left[1(1, {}_1) + 2(2, {}_2) + 3(3, {}_3) + \cdots + N(N, {}_n)\right],$$

$$b_1 = \frac{2}{n+1}\left[O(1, {}_1) + O(2, {}_2) + O(3, {}_3) + \cdots + O(N, {}_n)\right],$$

$$a_3 = \frac{2}{n+1}\left[1(1, {}_3) + 2(2, {}_6) + 3(3, {}_9) + \cdots + N(N, {}_{3n})\right],$$

$$b_3 = \frac{2}{n+1}\left[O(1, {}_3) + O(2, 6) + O(3, {}_9) + \cdots + O(N, {}_{3n})\right],$$

$$a_5 = \frac{2}{n+1}\left[1(1, {}_5) + 2(2, {}_{10}) + 3(3, {}_{15}) + \cdots + N(N, {}_{5n})\right],$$

$$b_5 = \frac{2}{n+1}\left[O(1, {}_{15}) + O(2, {}_{10}) + O(3, {}_{15}) + \cdots + N(N, {}_{5n})\right],$$

Usually it is not necessary to go further than this in the analysis of an actual wave. For example, the curves of Figs. 1 and 2 were plotted from the following data:

Angle.	e	Angle.	e	Angle.	e	Angle.	e
0	26	50	218	100	152	150	80
10	70	60	206	110	148	160	50
20	118	70	180	120	136	170	14
30	174	80	164	130	118	180	−26
40	210	90	154	140	100		

On analyzing the wave by the method of Fig. 3 (using $n + 1 = 18$), its equation was found to be

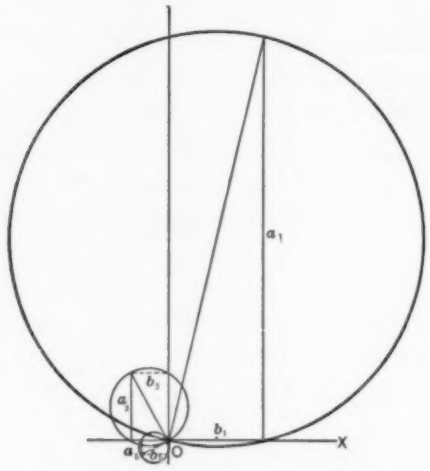


Fig. 4.

$$e = 191.4 \sin \omega t + 31.8 \sin 3\omega t - 6.9 \sin 5\omega t + 44.3 \cos \omega t - 17.5 \cos 3\omega t - 13.3 \cos 5\omega t.$$

In order to check the accuracy of the above equation, the curve which it represents was obtained, and plotted as a dashed line in Fig. 2; it can readily be seen that the two do not deviate appreciably.

In order to form an idea of the relative amplitudes and phase positions of the fundamental and harmonics we may make use of the fact that an equation of the form

$$e = a_1 \sin \omega t + a_3 \sin 3\omega t + a_5 \sin 5\omega t + \cdots + b_1 \cos \omega t + b_3 \cos 3\omega t + b_5 \cos 5\omega t + \cdots$$

may be written

(III)
$$e = \sqrt{a_1^2 + b_1^2} \cos\left(\omega t - \tan^{-1}\frac{a_1}{b_1}\right) + \sqrt{a_3^2 + b_3^2} \cos\left(3\omega t - \tan^{-1}\frac{a_3}{b_3}\right) + \sqrt{a_5^2 + b_5^2} \cos\left(5\omega t - \tan^{-1}\frac{a_5}{b_5}\right) + \cdots.$$

It is thus evident that the amplitude is in each case equal to the hypothenuse of a right triangle constructed on a and b as sides, and

that the phase position of this hypothenuse will be correctly shown if a and b are plotted along the vertical and horizontal, respectively, as in Fig. 4. Circles constructed on these hypothenuses will then represent the component sine waves in polar coördinates.

In recombining these components it must be remembered that corresponding vectors revolve with angular velocities which are to each other as 1 : 3 : 5 ; for example, if the vector of the fundamental occupies the position $x°$, the third and fifth harmonics will occupy positions $3x°$ and $5x°$, respectively. These angles are measured counter-clockwise from OX (Fig. 4), for which t in equation III. is zero.

In Fig. 1 the light lines represent these component curves in rectangular coördinates.

ITHACA, N. Y., February, 1901.

NEW BOOKS.

Photometrical Measurements. By WILBUR M. STINE. 12mo., 270 pp., 67 illustrations. New York, The Macmillan Co., 1900.

This work, as the subtitle indicates, deals almost exclusively with the photometry of arc and incandescent lights. This would seem to be a matter for regret, as there is no good reason why a manual of "Photometrical Measurements," written with especial regard to the needs of the practician, should not dwell with appropriate fullness upon the peculiar features, which are not a few, of the photometry of oil and gas sources.

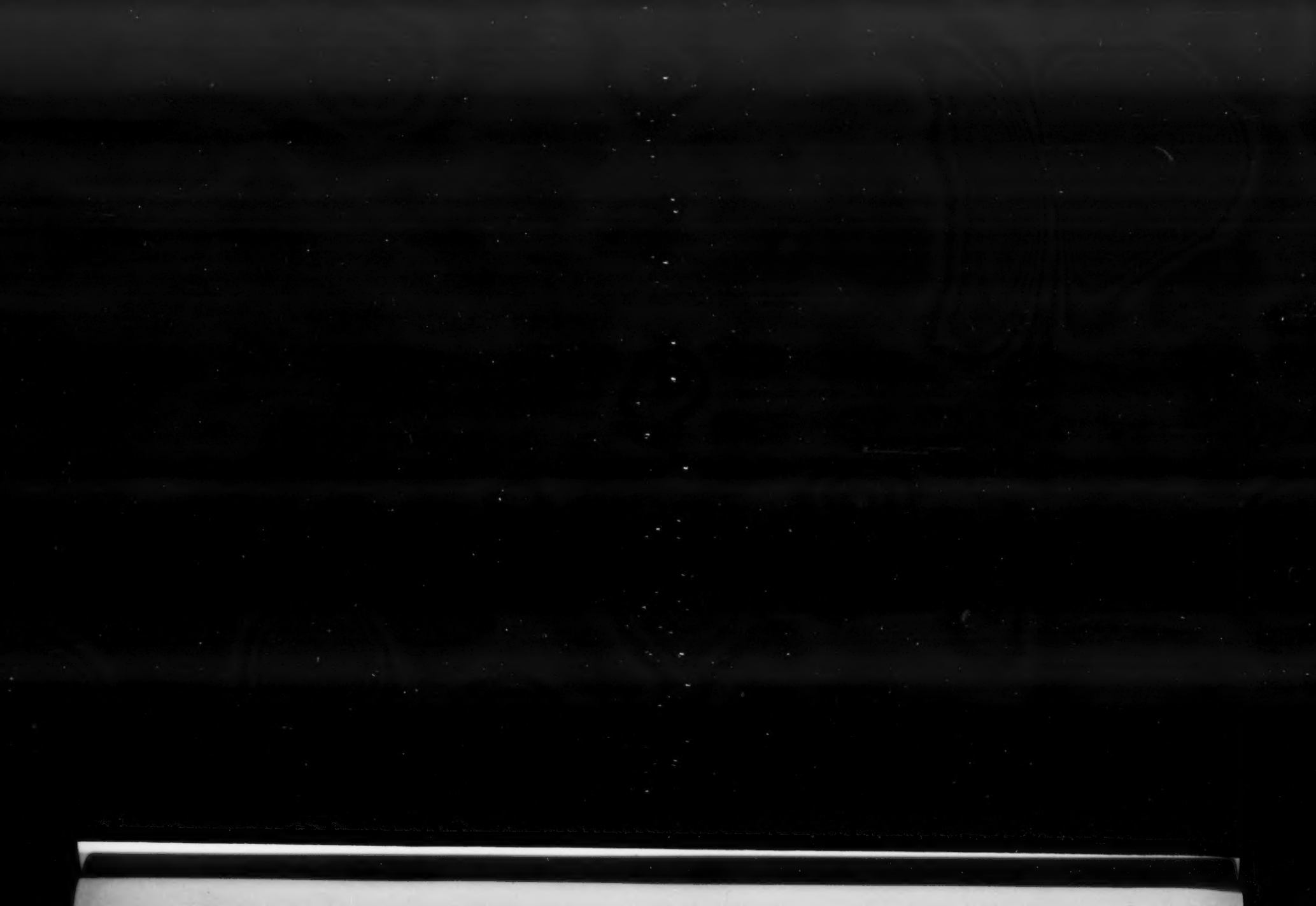
The author presents his subject-matter in topical form, which makes the book convenient for reference use. Original sources are frequently referred to—a very commendable feature. In this respect the author has avoided what seems to be a growing tendency among end-of-the-century writers of the technical manual, namely, a tendency towards a fine disregard for sources of information, which manifests, in a work essentially a compilation, more brevity than courtesy. One reads in the preface that the work has been written "from the literature of photometry and with little reference to existing works on the subject." This, of course, is as it should be.

Chapter I. deals with such physical and physiological light phenomena as are likely to enter into ordinary photometric practice. The next chapter, which through a typographical error is also numbered I., treats of the laws of distance and inclination, of *illumination*, *intrinsic brightness* and other fundamental notions. The author argues well for the abandonment of the name *candle-power* and the substitution of the name *light unit* pending the development of a satisfactory light standard. The author considers the *quantity of light* emitted by a source of intensity I as $4\pi I$ units, as does Palaz in his well-known treatise. Blondel, on the other hand, calls this magnitude *luminous flux*, while reserving the term *quantity of light* for the product flux $\times$ time. This latter usage has much to commend it, both by way of physical analogy and practical value. The concept of flux $\times$ time, or more often, intensity $\times$ time, is used constantly by practical men under the guise of *candle-power hours*, and is of evident utility. Whether we are ready or not ready for a new word for each photometric quantity, there can be no question as to the need of having a given term mean one thing and one thing only.

In his discussion of the method of finding the mean spherical intensity from a meridional section of the photometric surface, the author makes a serious blunder. One is told to take the area of the given polar distribution curve and to draw a circle of equal area. The radius of this circle is the value sought! Had the author written the usual expression for the area of a polar curve instead of the double integral of equation (39), he could hardly have failed to note that the area of such a curve is a function of the square of the radius vector and hence the equivalent circle has a radius equal to $\surd$ mean square. To borrow from the terminology of alternating currents, this process leads to the *virtual candle-power*. It is doubtful if our most enthusiastic advocates of a revised photometric nomenclature are prepared for this. In the hypothetical distribution curve given as an example, namely two circles tangent at a given point in a vertical line this method leads to .707 × maximum intensity, whereas the true mean spherical intensity $[\frac{1}{2}\int_0^{\pi} I_\theta \sin\theta d\theta]$ is .785 × the maximum intensity. Again, in Art. 231, the reader is told to obtain the mean spherical intensity of a glow lamp by the same erroneous method. In Appendix A, which deals with the results of Williamson and Klinck on the absorption of various globes over a mantle burner, the author says: "* * * the mean spherical candle-power was calculated by the methods already explaimed." The figures accompanying the text show plainly that the integration was performed by the classic method of the Rousseau diagram.

The subjects of Photometers and Light Standards are taken up in an able manner in Chapters III. and IV. These two chapters cover a good half of the book and furnish an excellent *résumé* of the subjects, without too great description of apparatus whose value is chiefly historical. Naturally, the greatest prominence is given to the Bunsen and Lummer-Brodhun screens, and to the amyl acetate standard. No mention is made of the very carefully elaborated Blondel-Broca universal photometer. Article 179 on the working values of light standards will prove very useful to one who wishes to compare the results of different observers. The author neglects to state in this connection that the Geneva Congress (1896) decided that, for practical purposes, the *bougie décimale* would be considered as represented by the Hefner lamp.

In Chapter VI. the photometry of the glow lamp is well discussed. The concluding chapter on arc-light photometry is hardly as complete as one could wish for. The devices designed by Houston and Kennelly and by Blondel for giving directly the mean spherical intensity might well be given some notice here.

As a whole the work will be useful to students of the subject, but the errors to which attention has been called should receive early correction.

C. P. MATTHEWS.